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(54) **Thermosetting resin compositions and their manufacture**

Wärmehärtende Harzzusammensetzungen und ihre Herstellung

Compositions de résines thermodurcissables et leur fabrication

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(56) References cited:
DE-A- 4 028 845 **FR-A- 2 355 049**
US-A- 4 902 778

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The file contains technical information submitted
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Description

[0001] This invention relates to thermosetting resin compositions and methods of making and using them. In preferred aspects it is concerned particularly with achieving good workability and heat resistance.

BACKGROUND

[0002] Thermosetting resin compositions have been widely used as a variety of electrically insulating materials, structural materials, and adhesives by molding, casting, impregnating, laminating, and other forming techniques. Increasingly rigorous requirements are currently imposed in these applications, among which heat resistance is important.

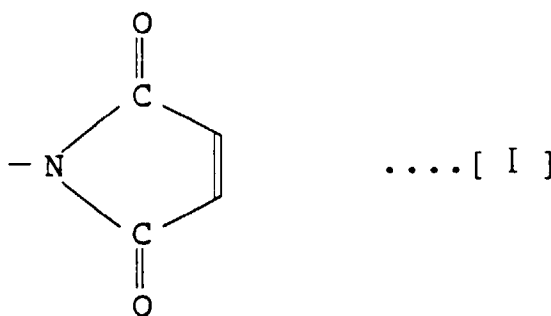
[0003] Typical thermosetting resin compositions include polyimide and epoxy resins. The polyimide resins have satisfactory heat resistance, but are poorly workable in that they require prolonged heating at high temperatures for working. The epoxy resins modified to improve heat resistance are easily workable, but insufficient in mechanical and electrical properties at high temperatures, long-term thermal degradation resistance, and extreme heat resistant function.

[0004] Several replacements have been proposed e.g. a thermosetting resin mixture comprising a polyimide and an alkenyl phenol or alkenyl phenol ether as disclosed in Japanese Patent Application KoKai (JP-A) No. 994/1977, and a heat resistant resin composition comprising a maleimide compound, a polyallylated phenol, and an epoxy resin as disclosed in Japanese Patent Publication No. 28416/1982. Since the polyallylated phenol used in the latter composition has a structure in which a polyallyl ether compound has been subject to Claisen rearrangement or Claisen rearrangement creates a phenolic hydroxyl group during heat curing, each substituting allyl group and a hydroxyl or ether group are at ortho-positions on a common aromatic ring and they would remain unreacted after curing especially in the case of novolak type resin compositions, leaving problems in cured properties and thermal degradation resistance at high temperatures.

[0005] US-A-4 902 778 discloses the use of a toughener derived from an epoxy resin to increase the toughness of bismaleimide resins.

[0006] Our broad aim herein is to provide novel thermosetting compositions together with ways of making and using them. In preferred aspects we seek to address the problem of providing one or more of good resin workability, and good heat resistance, low thermal expansion, and low water absorption in the cured product.

[0007] Making investigation on a thermosetting resin composition comprising (A) an imide compound having a maleimide group of the general formula [I] shown below, (B) a resin having at least two epoxy groups in a molecule, and (C) a resin having a phenolic hydroxy group in a molecule, the inventors have found that when resin (B) has a double bond conjugated with a naphthalene ring, they were able to obtain good workability and curing to products having good adhesion, good high-temperature mechanical strength, hot water resistance, low thermal expansion, and low water absorption.



[0008] It is generally known that compounds having a maleimide group are effective for imparting heat resistance, but thermosetting resin compositions having such imide compounds blended therein are poor in long-term heat resistance, adhesion, and workability. In contrast, according to the present teachings, component (B) having a double bond conjugated with a naphthalene ring is used in combination with an imide compound having a maleimide group. Then an unsaturated bond in the maleimide ring of the imide compound reacts with the double bond conjugated with a naphthalene ring to form a copolymer. The copolymer formation, coupled with the effect of naphthalene ring included, is believed to give these compositions the good properties referred to above.

[0009] The inventors have also found that a thermosetting resin composition comprising components (A), (B), and

(C) may be reduced in stress by adding thereto a copolymer obtained by reacting an aromatic polymer with an organopolysiloxane having the compositional formula [II].

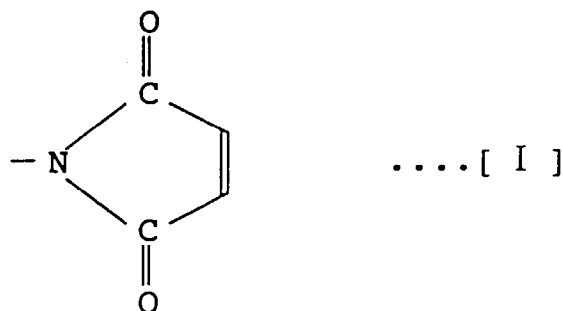


In formula [II], R^1 is a hydrogen atom, hydroxyl group, alkoxy group, or monovalent organic group containing an amino, epoxy, hydroxyl or carboxyl group, R^2 is a substituted or unsubstituted monovalent organic group, and letters a and b are positive numbers satisfying $0.001 \leq a \leq 1$, $1 \leq b \leq 3$, and $1.001 \leq a + b \leq 4$. The number of silicon atoms said organopolysiloxane has in its molecule is an integer of 1 to 1000. The number of functional groups represented by R^1 directly attached to silicon atoms of said organopolysiloxane in its molecule is an integer of at least 1.

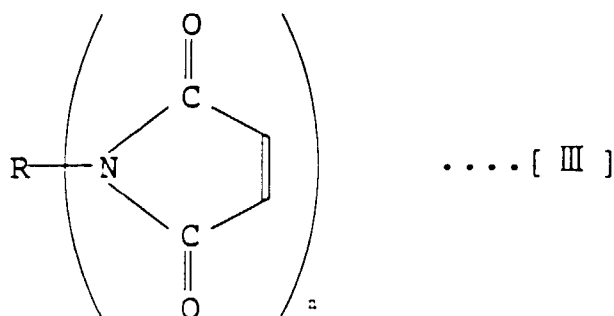
[0010] In one aspect, therefore, we provide a thermosetting resin composition comprising (A) an imide compound having a maleimide group of formula [I], (B) a resin having at least two epoxy groups in a molecule, and (C) a resin having a phenolic hydroxyl group in a molecule, component (B) having a double bond conjugated with a naphthalene ring, and the composition optionally further containing (D) a copolymer obtainable by reacting an aromatic polymer with an organopolysiloxane having formula [II].

[0011] In other aspects, we provide methods comprising the preparation of such compositions, and their use for moulding, adhesion, coating or encapsulating.

[0012] Component (A) in the thermosetting resin composition of the present invention is an imide compound having at least one maleimide group of formula [I].

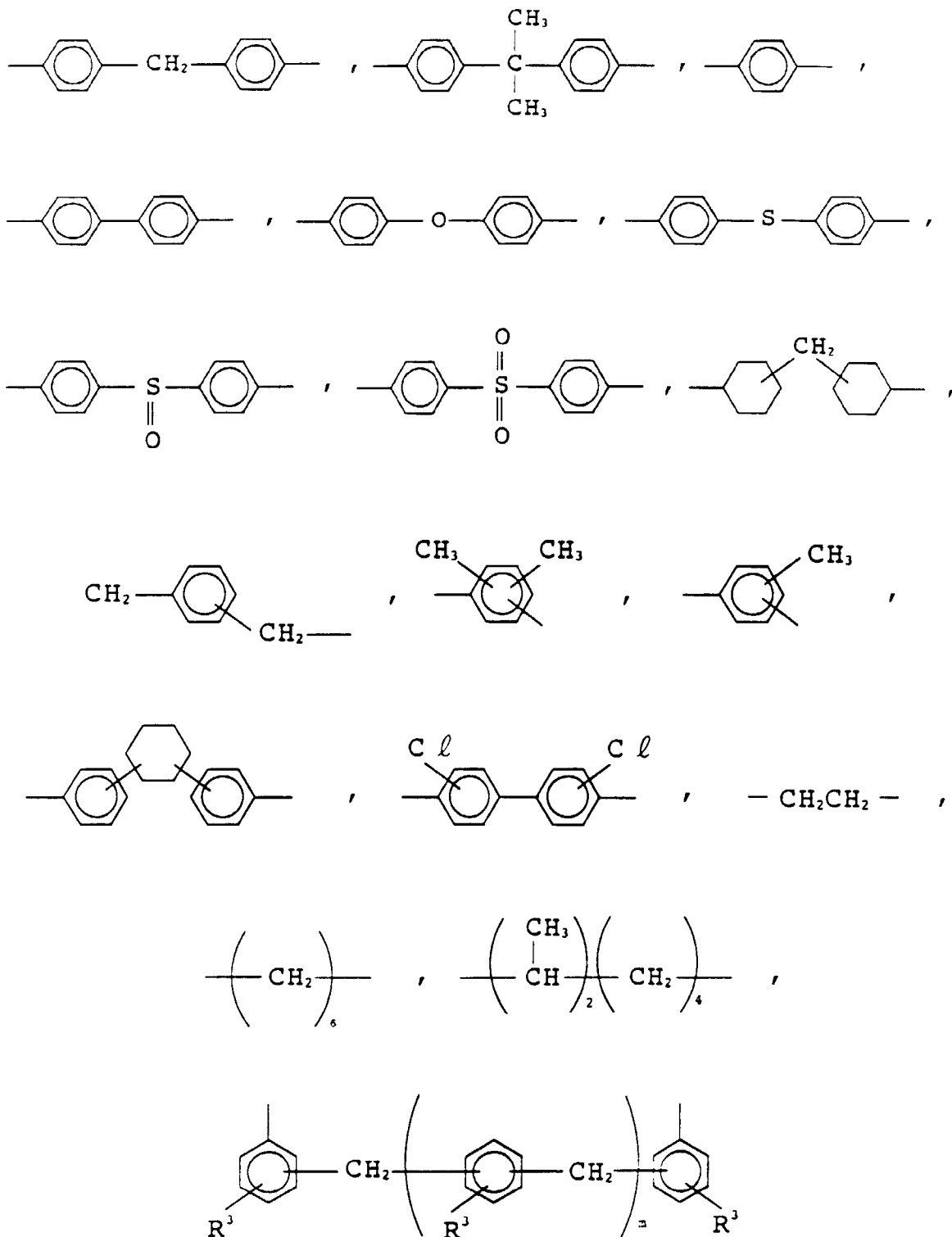


[0013] In the practice of the invention, preferred among the imide components are those having an N-substituted maleimide group of the following formula [III].



In formula [III], substituent R is an n -valent organic group, and n is an integer of from 1 to 20, preferably from 2 to 7, most preferably equal to 2.

[0014] Where n is equal to 2, the divalent organic group R is preferably selected from halogen substituted or unsubstituted divalent aliphatic hydrocarbon groups having 1 to 20 carbon atoms, halogen substituted or unsubstituted divalent aromatic hydrocarbon groups having 6 to 20 carbon atoms, halogen substituted or unsubstituted alkylene arylene groups having 7 to 20 carbon atoms, and corresponding divalent organic groups having a functional group such as an ether, thioether, sulfoxide, and sulfone group. Several illustrative examples of substituent R are given below.

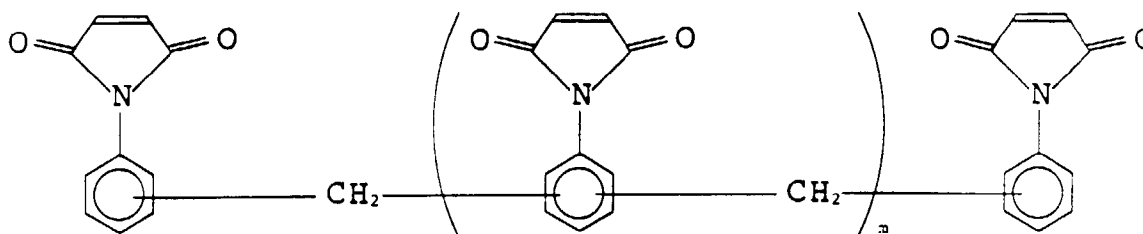


In the last formula, R^3 is a hydrogen atom, halogen atom or alkyl group having 1 to 4 carbon atoms, and m is an integer of from 0 to 18.

[0015] Examples of the compound having an N-substituted maleimide group include N,N'-bis-maleimides such as N,N'-diphenylmethanebis-maleimide, N,N'-phenylenebismaleimide, N,N'-diphenyletherbismaleimide, N,N'-diphenylsulfonebismaleimide, N,N'-dicyclohexylmethanebismaleimide, N,N'-xylenebismaleimide, N,N'-tolylenebismaleimide, N,N'-xylenebismaleimide, N,N'-diphenylcyclohexanebismaleimide, N,N'-dichlorodiphenylbismaleimide, N,N'-diphenylmethanebismethylmaleimide, N,N'-diphenyletherbismethylmaleimide, N,N'-diphenylsulfonebismethylmaleimide, N,N'-

ethylenebismaleimide, N,N'-hexamethylenebismaleimide, and N,N'-hexamethylenebismethylmaleimide (all inclusive of isomers); prepolymers terminated with an N,N'-bismaleimide skeleton obtained by adding these N,N'-bismaleimides to diamines; and maleimide and methylmaleimide compounds of aniline and formalin condensates.

[0016] Other useful imide compounds include compounds of the formula shown below and mixtures of an N-substituted monomaleimide, N-substituted trimaleimide or N-substituted tetramaleimide and an N-substituted bismaleimide.

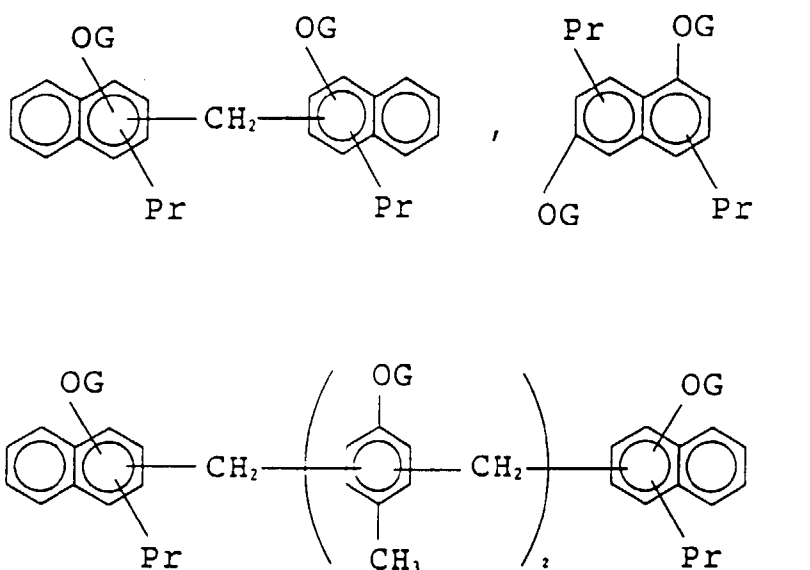


[0017] Also acceptable are the foregoing maleimide compounds modified with silicones.

[0018] In the practice of the invention, the imide compounds may be used alone or in admixture of two or more. Preferred among others are N-substituted trimaleimides and N-substituted bismaleimides, especially N,N'-diphenylmethanebismaleimide.

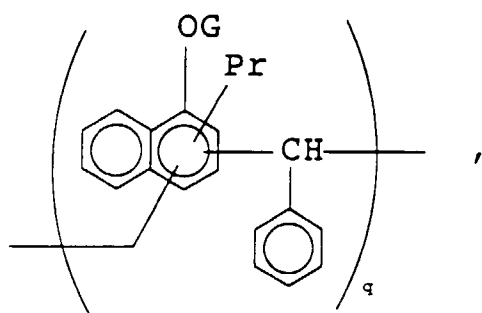
[0019] Component (B) is an epoxy resin having at least two epoxy groups in a molecule and wherein component (B) has a double bond conjugated with a naphthalene ring. The resulting thermosetting resin composition will cure to products having a low coefficient of expansion and low moisture absorption.

[0020] Examples of the epoxy resin (B) having a naphthalene ring are given below.



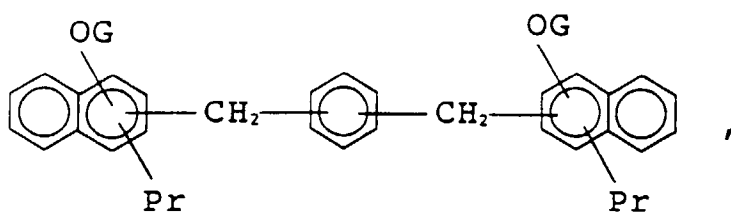
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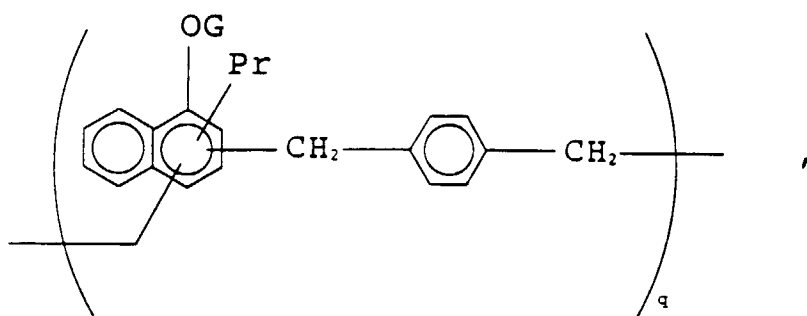
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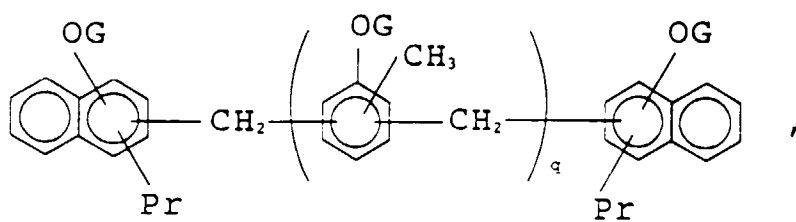
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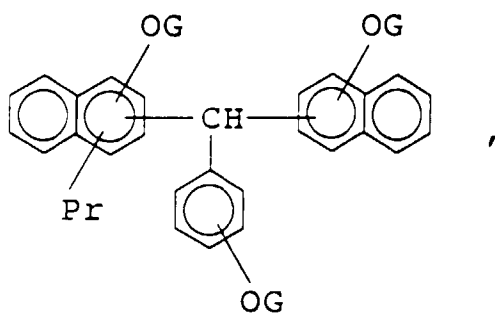
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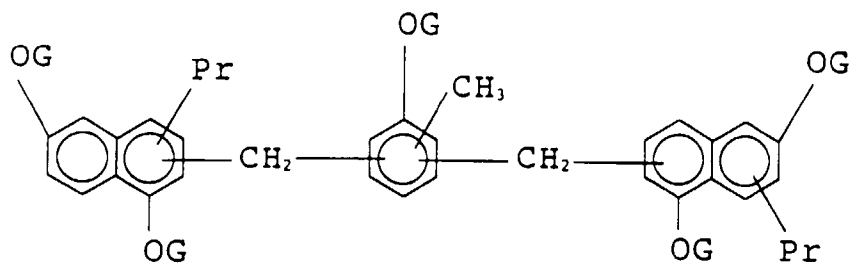


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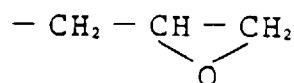
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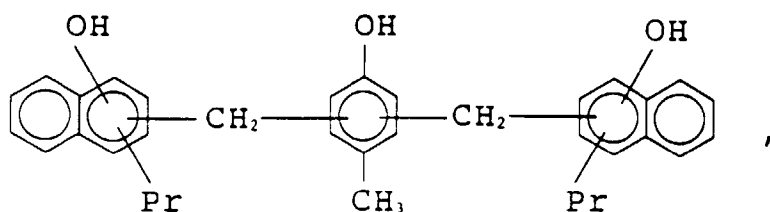
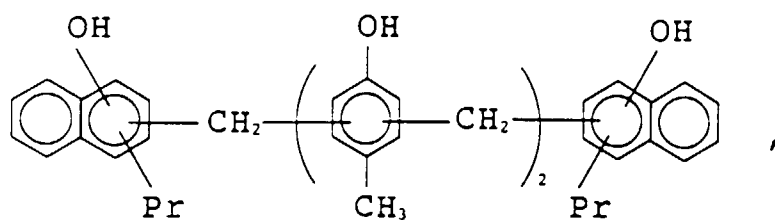
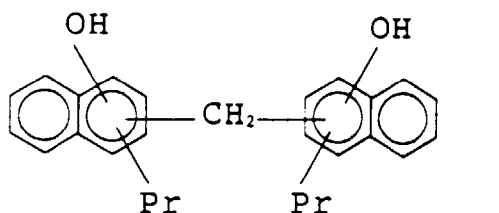
Pr: -CH=CH-CH₃

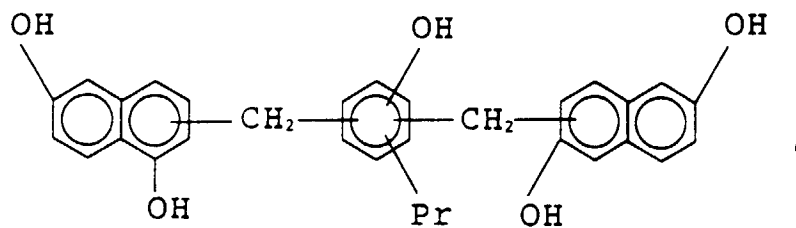
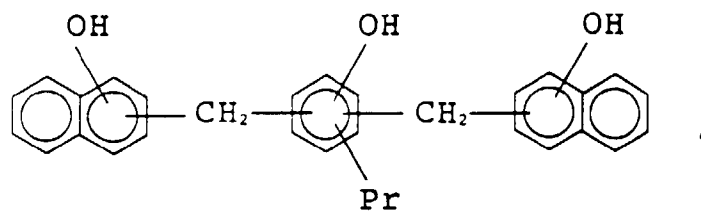
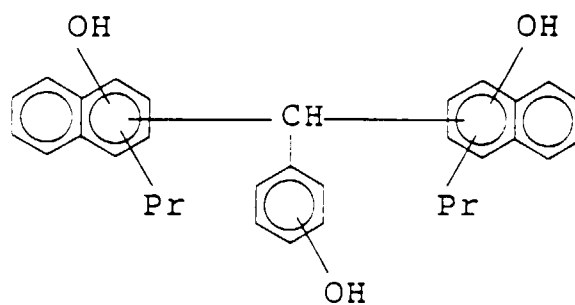
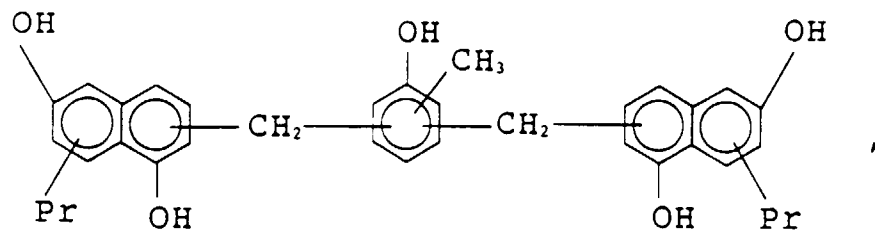
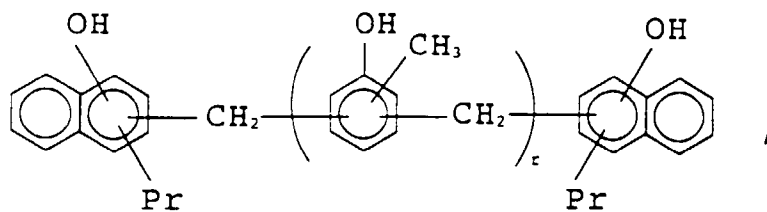
q: an integer of from 2 to 10

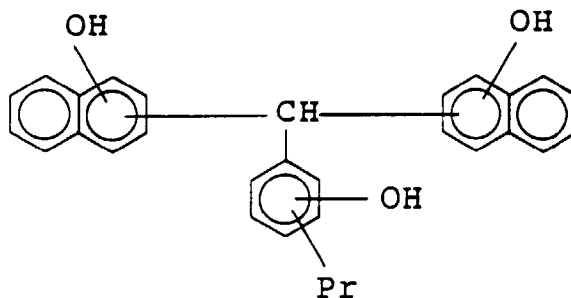
[0021] The epoxy resin may be used alone or in admixture of two or more.

[0022] Component (C) is a resin having a phenolic hydroxyl group in a molecule which serves as a curing agent. Included are phenolic resins such as novolak type phenolic resins, resol type phenolic resins, triphenol alkane type resins, naphthol type resins, and biphenyl type phenolic resins; and phenolic resins having at least one double bond conjugated with an aromatic ring (e.g., substituted or unsubstituted benzene or naphthalene ring) in a molecule and at least one substituted or unsubstituted naphthalene ring in a molecule. The phenolic resins may be used alone or in admixture of two or more. Preferred among these phenolic resins are phenolic resins having a double bond conjugated with an aromatic ring and a naphthalene ring in a molecule because the resulting thermosetting resin composition cures to products having a low coefficient of expansion, a high glass transition temperature (T_g), a low modulus of elasticity at temperatures above T_g, and minimal moisture absorption.

[0023] Examples of the phenolic resin having a naphthalene ring are given below.







Pr: -CH=CH-CH₃

r: an integer of from 1 to 10

[0024] The epoxy and phenolic resins each having a double bond conjugated with an aromatic ring and a naphthalene ring in a molecule may be synthesized by conventional methods, for example, simply by reacting a phenolic resin with an allyl ether and subjecting the allyl etherified phenolic resin to Claisen rearrangement and then to isomerization.

[0025] In the composition of the invention, the total amount of components (B) and (C) blended preferably ranges from about 20 to about 400 parts, more preferably from about 50 to about 300 parts by weight per 100 parts by weight of component (A) or imide compound. Less than 20 parts of components (B) and (C) combined would sometimes result in cured products having poor workability and heat resistance whereas more than 400 parts of components (B) and (C) combined would lead to lower T_g and poor long-term heat resistance.

[0026] Desirably, components (B) and (C) contain epoxy and phenolic hydroxyl groups in such quantities that the ratio of the quantity of epoxy group (a mol) to the quantity of phenolic hydroxyl group (b mol), a/b, ranges from 1/2 to 3/2. Outside the range, curing property and low stress are sometimes lost.

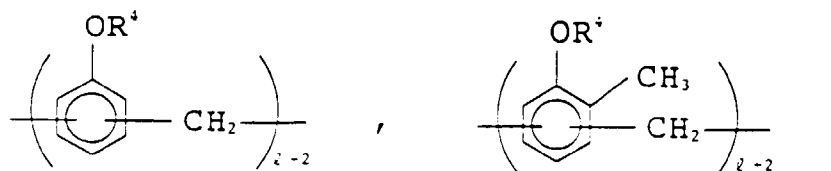
[0027] The composition of the invention is a blend comprising components (A), (B), and (C) as defined above. Components (C) may have a double bond conjugated with an aromatic group and a naphthalene ring.

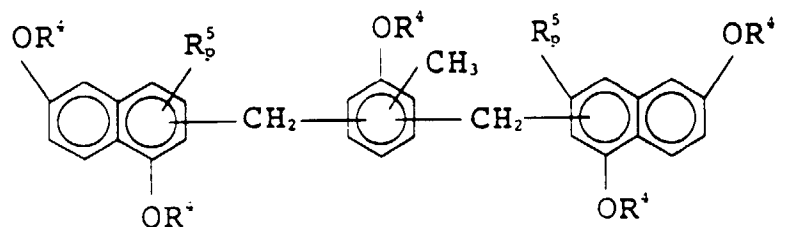
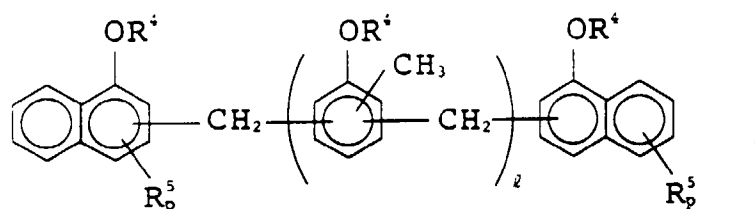
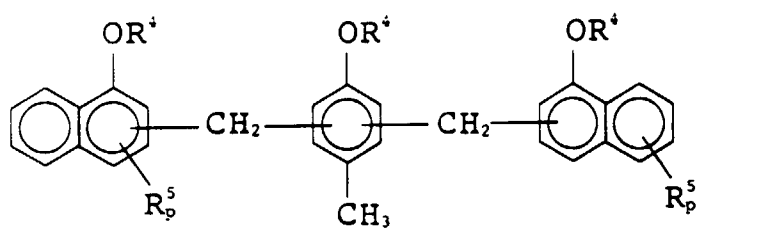
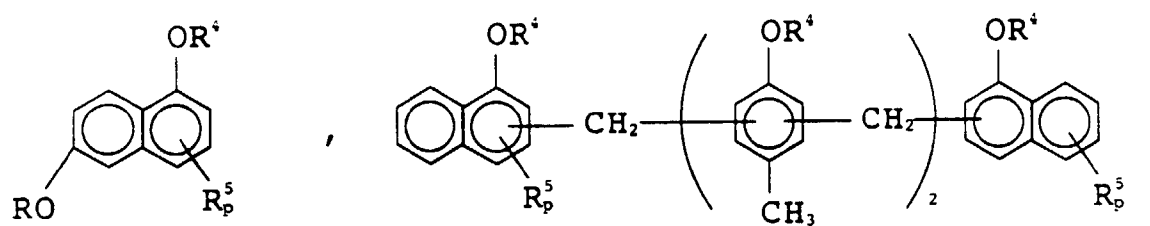
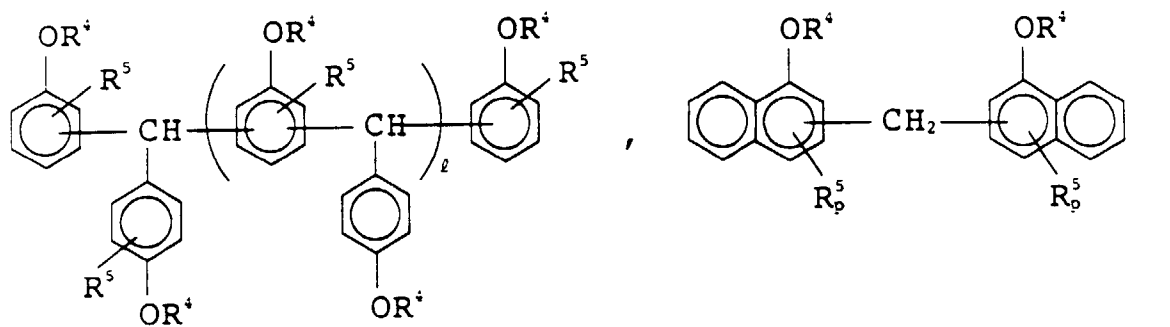
[0028] Preferably, the naphthalene ring, which is either substituted or unsubstituted, is contained in an amount of at least 10% by weight based on components (B) and (C) combined. With a naphthalene ring content of less than 10% by weight, the resulting cured products tend to be less good in crack resistance since the moisture absorption and the modulus of elasticity in a temperature range above T_g are insufficiently reduced. With a naphthalene ring content of more than 80% by weight, problems may arise with respect to dispersion upon preparation and moldability.

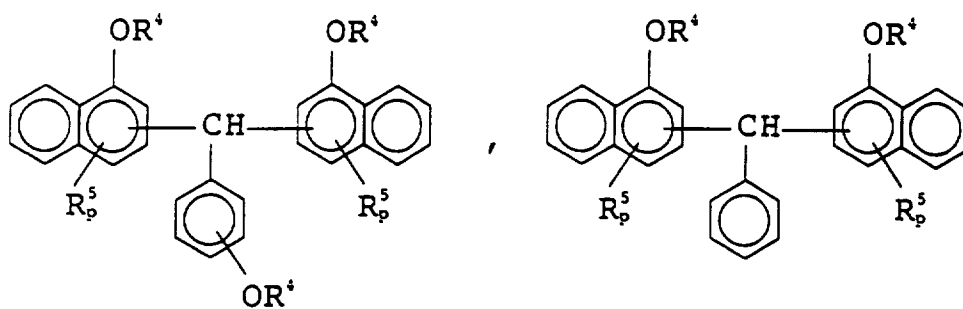
[0029] Further it is preferred in the practice of the invention that the functional group ratio B'/A' range from 0.1 to 2, especially from 0.3 to 1, provided that component (A) or imide compound contains A' mol of a vinyl group and components (B) and (C) contain B' mol (in total) of a vinyl group as a double bond conjugated with an aromatic ring. If functional group ratio B'/A' exceeds 2, that is, the vinyl group as the conjugated double bond is present in a larger proportion, curing difficulties may arise in that a larger portion is left unreacted, curing to less reliable products having poor long-term heat resistance. If B'/A' is less than 0.1, that is, the vinyl group as the conjugated double bond is present in a smaller proportion, there may arise problems of moldability and mechanical strength.

[0030] For imparting low stress property to the compositions, we have found it advantageous to further blend (D) a copolymer obtained by reacting an aromatic polymer with a specific organopolysiloxane.

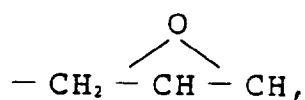
[0031] The aromatic polymer used herein may be selected from various compounds, for example, compounds having the following structural units.





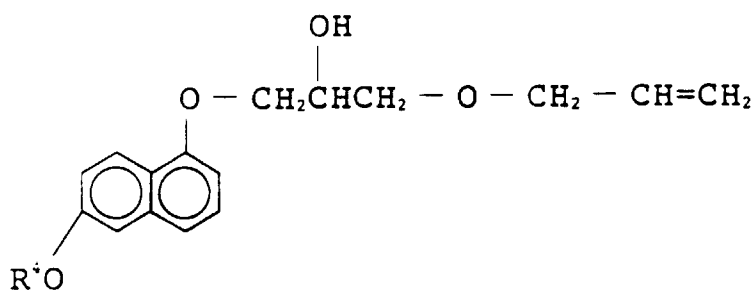
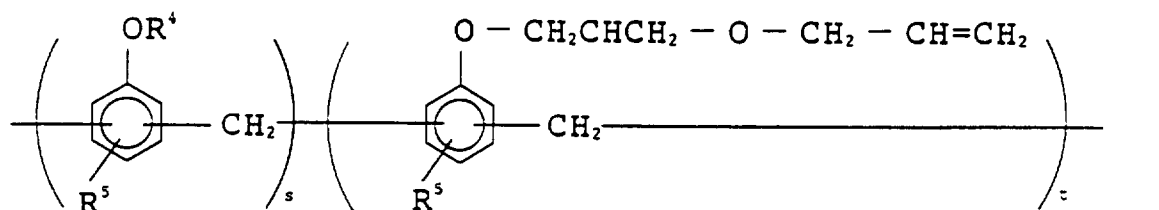
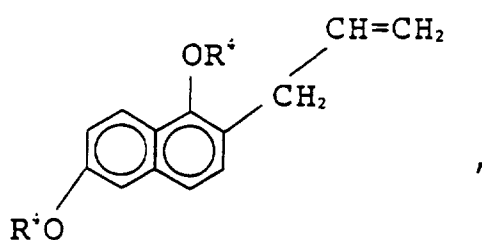


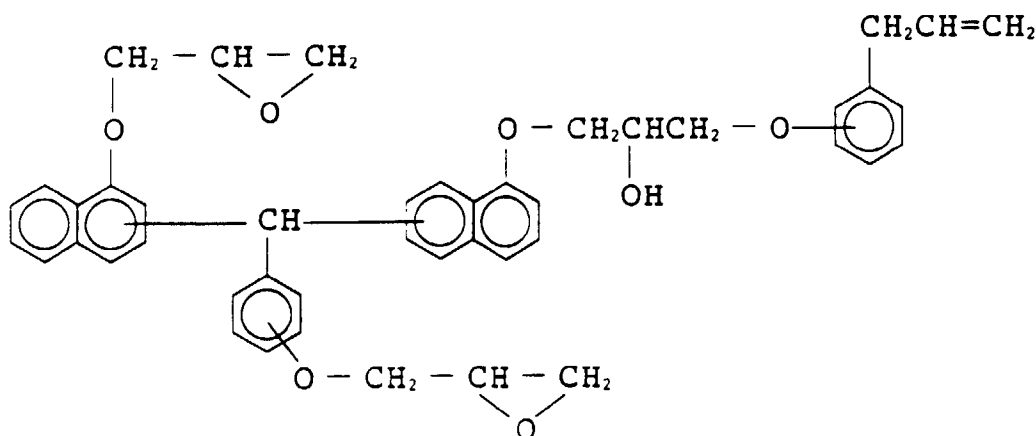
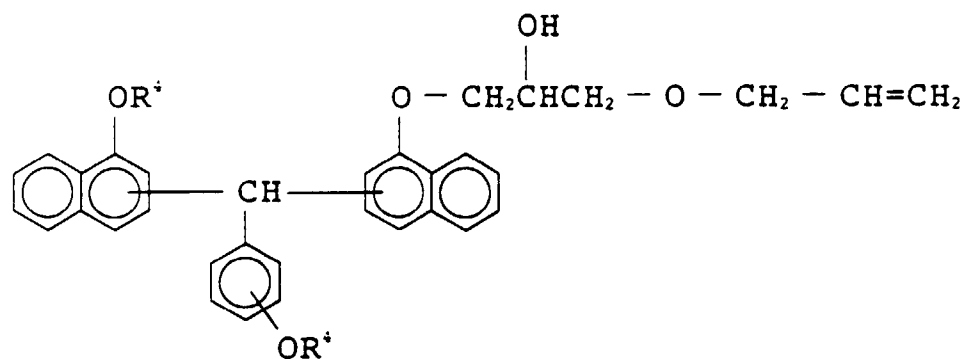
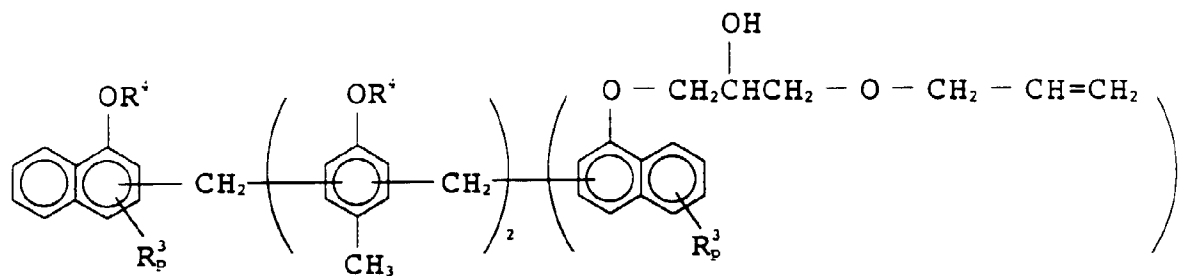
In the formulae, R^4 is a hydrogen atom or



R^5 is independently selected from alkyl groups having 1 to 10 carbon atoms, ℓ is an integer of from 0 to 4, and p is an integer of from 0 to 2.

[0032] Other useful aromatic polymers are naphthalene resins having an alkenyl group as shown by the following formulae.





In the formulae, s and t each is an integer of from 1 to 6.

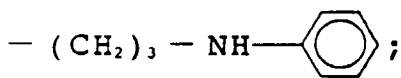
[0033] The alkenyl group - containing naphthalene resins may be synthesized by conventional methods, for example, simply by reacting a naphthalene skeleton - containing phenolic resin with allyl glycidyl ether for introducing an alkenyl group into its molecule, or by partially reacting a naphthalene skeleton - containing epoxy resin with 2 - allylphenol or the like.

[0034] The other reactant, organopolysiloxane has the compositional formula [II]:

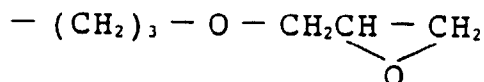


wherein R^1 is a hydrogen atom, hydroxyl group, alkoxy group, or monovalent organic group containing an amino, epoxy, hydroxyl or carboxyl group, R^2 is a substituted or unsubstituted monovalent organic group, and letters a and b are positive numbers satisfying $0.001 \leq a \leq 1$, $1 \leq b \leq 3$, and $1.001 \leq a + b \leq 4$. The number of silicon atoms the organopolysiloxane has in its molecule is an integer of 1 to 1000. The number of functional groups represented by R^1 directly attached to silicon atoms of the organopolysiloxane in its molecule is an integer of at least 1.

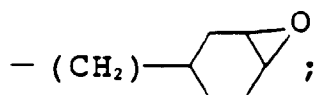
[0035] Examples of substituent R¹ include a hydrogen atom; a hydroxyl group; alkoxy groups such as methoxy, ethoxy, propoxy, isopropoxy, butoxy, methoxyethoxy, and ethoxyethoxy groups; amino group-containing organic groups such as - (CH₂)₃NH₂, - (CH₂)₃-NHCH₂CH₂NH₂, and



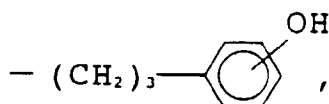
epoxy group-containing organic groups such as



and



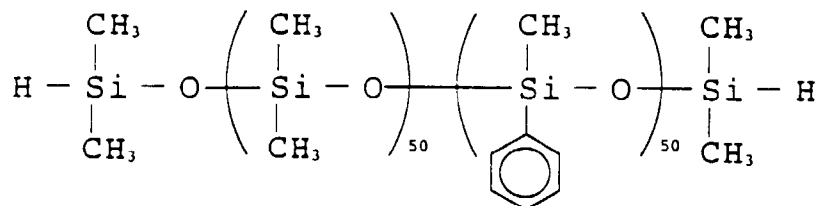
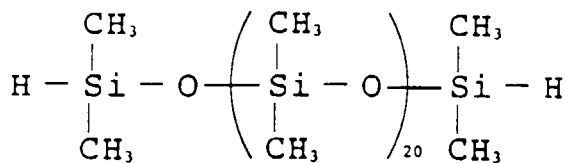
hydroxyl group-containing organic groups such as -CH₂OH and

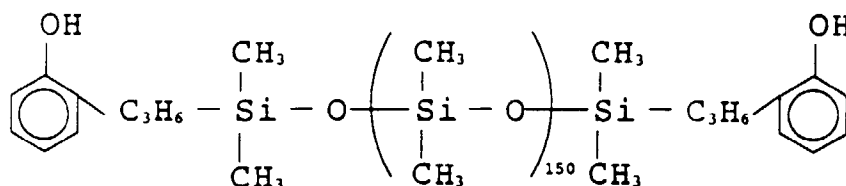
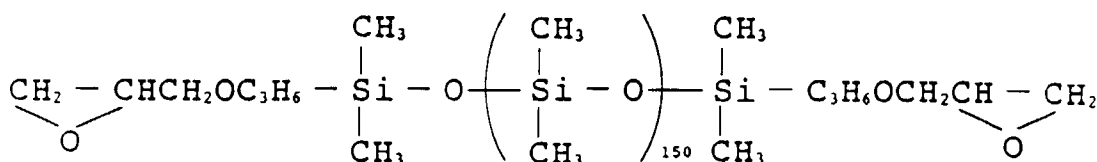
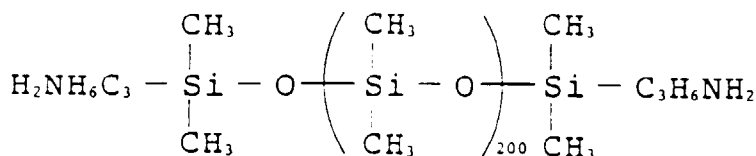
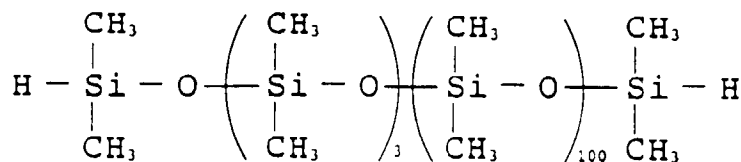


preferably organic groups containing a phenolic hydroxyl group; and carboxyl group-containing organic groups such as -(CH₂)_u-COOH wherein u is an integer of from 1 to 8.

[0036] The substituent R² is a substituted or unsubstituted monovalent organic group having 1 to 10 carbon atoms, for example, alkyl groups such as methyl, ethyl, propyl, and butyl groups; alkenyl groups such as vinyl and allyl groups; cycloalkyl groups such as cyclohexyl group; aryl groups such as phenyl and tolyl groups; aralkyl groups such as benzyl and phenylethyl groups; and substituted ones thereof in which some or all of the hydrogen atoms are replaced by halogen atoms or the like, such as chloromethyl and 3,3,3-trifluoropropyl groups.

[0037] Illustrative examples of the organopolysiloxane of formula [II] are given below.





[0038] Although the molecular weight is not critical, the organopolysiloxane of formula [II] preferably has a molecular weight of about 100 to about 70,000. This molecular weight range is selected because when the aromatic polymer-organopolysiloxane copolymer is blended in the thermosetting resin composition, the copolymer is not miscible in the matrix, but forms a fine island-in-sea structure. With an organopolysiloxane molecular weight of less than 100, the resulting copolymer would be less effective for imparting flexibility or high Tg to the thermosetting resin composition when blended therein. With an organopolysiloxane molecular weight of more than 70,000, the resulting copolymer tends to become incompatible with the thermosetting resin composition, resulting in cured products having the copolymer separated and poor physical properties (flexural strength).

[0039] The copolymer is preferably blended in an amount of 2 to 100 parts by weight per 100 parts by weight of the total of components (A), (B) and (C). Less than 2 parts by weight may result in cured products having poor crack resistance, whereas more than 100 parts by weight may result in cured products having poor mechanical strength although the products have good crack resistance.

[0040] The copolymer between the aromatic polymer and the organopolysiloxane of formula [II] may be prepared by effecting addition reaction between them according to conventional methods. Addition reaction between the aromatic polymer and the organopolysiloxane of formula [II] is preferably effected in an inert solvent such as benzene, toluene, and methyl isobutyl ketone using a catalytic amount of any desired one of well-known addition catalysts, for example, platinum catalysts, typically chloroplatinic acid. The reaction temperature is not critical although a temperature of about 60 to 120°C is preferred. Usually, reaction continues for about 30 minutes to about 24 hours. Copolymers between an aromatic polymer and an aminopolysiloxane or epoxypolysiloxane may be obtained by reacting the reactants at room temperature or elevated temperature. A suitable solvent such as methyl isobutyl ketone, toluene, dioxane or methyl "Cellosolve®" is desirably used in order to mix the reactants uniformly or nearly uniformly. For promoting the reaction, water, alcohols such as butanol, isopropyl alcohol and ethanol, and phenols may be used. It is also desirable to use

reaction catalysts, for example, amines such as tributyl amine and 1,8-diazabicycloundecene-7, organic phosphines such as triphenylphosphine, and imidazoles such as 2-phenylimidazole.

[0041] In order to complete the crosslinkage between the imide compound having a maleimide group of formula [I] and a resin having a double bond conjugated with an aromatic group, a curing catalyst is preferably blended in the composition of the invention. Useful curing catalysts are organic peroxides including benzoyl peroxide, para-chlorobenzoyl peroxide, 2,4-dichlorobenzoyl peroxide, capryl peroxide, lauroyl peroxide, acetyl peroxide, methyl ethyl ketone peroxide, cyclohexanone peroxide, bis(1-hydroxycyclohexyl peroxide), hydroxyheptyl peroxide, tert-butyl hydroperoxide, p-methane hydroperoxide, cumene hydroperoxide, di-tert-butyl peroxide, dicumyl peroxide, 2,5-dimethyl-2,5-di(tert-butyl peroxide)hexane, 2,5-dimethylhexyl-2,5-di(peroxybenzoate), tert-butyl perbenzoate, tert-butyl peracetate, tert-butyl peroctoate, tert-butyl peroxyisobutyrate, and di-tert-butyl diperphthalate alone and mixtures thereof.

[0042] Further, it is preferred to use various curing promoters for the purpose of promoting the reaction between the curing catalyst and the resins. Useful curing promoters include organic phosphines, for example, triphenyl phosphine, tricyclohexyl phosphine, tributyl phosphine, methyl diphenyl phosphine, 1,2-bis(diphenylphosphino)ethane, and bis(diphenylphosphino)-methane; tertiary amines, for example, 1,8-diazabicyclo[5.4.0]undecene-7; and imidazoles. They may be used alone or in admixture of two or more.

[0043] The curing catalyst and curing promoter are used in a total amount of about 0.01 to 10 parts, especially about 0.1 to 2 parts by weight per 100 parts by weight of components (A), (B), (C) and (D) combined. A catalyst and promoter amount of less than 0.01 parts is not effective for curing promotion whereas more than 10 parts of the catalyst and promoter would cause the composition to cure too fast and adversely affect its moldability.

[0044] If desired, the composition of the invention may further contain an inorganic filler. The inorganic filler is selected from fillers commonly blended in thermosetting resin compositions, for example, silicas such as fused silica and crystalline silica, alumina, carbon black, mica, clay, kaolin, glass beads, glass fibers, aluminum nitride, silicon carbide, zinc oxide, antimony trioxide, calcium carbide, aluminum hydroxide, beryllium oxide, boron nitride, titanium oxide, silicon carbide, and iron oxide.

[0045] These inorganic fillers may be used alone or in admixture of two or more. The filler is preferably used in an amount of about 100 to about 1,000 parts, especially about 200 to about 700 parts by weight per 100 parts by weight of the total of components (A), (B), (C), and (D) although the filler content is not particularly limited.

[0046] The composition of the invention may further contain various other additives if desired. Exemplary well-known additives include thermoplastic resins, thermoplastic elastomers, organic synthetic rubbers, silicone gel or cured silicone rubber powder; mold release agents such as waxes (e.g., carnauba wax) and fatty acids (e.g., stearic acid) and metal salts thereof; pigments such as carbon black, cobalt blue, and red iron oxide; flame retardants such as antimony oxide and halides; surface treating agents such as silanes (e.g., γ -glycidoxypolytrimethoxysilane); coupling agents such as epoxy silanes, vinyl silanes, boron compounds and alkyl titanates; antioxidants; other additives, and mixtures thereof.

[0047] The compositions may generally be prepared by admixture of components, particularly by mixing and agitating predetermined amounts of the necessary components uniformly, and milling the mixture in milling means preheated at 70 to 95°C, for example, a kneader, roll mill and extruder, followed by cooling and comminution. The order of mixing the components is not critical.

[0048] Compositions embodying the invention are advantageously applicable as molding materials, powder coating materials, and adhesives. The compositions are also useful in encapsulating various semiconductor devices including IC, LSI, transistors, thyristors and diodes and manufacturing printed circuit boards.

[0049] Using the teachings herein it is possible to make compositions which cure into low stressed products having improved adhesion and workability, mechanical strength at elevated temperatures, hot water resistance, heat resistance and low water absorption. Such compositions are useful in view of current service requirements of thermosetting resin compositions and are useful as various electrically insulating materials, structural materials, adhesives, powder coating materials, and semiconductor encapsulants.

EXAMPLE

[0050] Examples of the present invention are given below together with comparative examples. All parts are by weight.

Examples 1 - 14 and Comparative Examples 1 - 6

[0051] Thermosetting resin compositions were prepared by uniformly melt mixing the following components in a hot two-roll mill. The components used were 30 parts of N,N'-4,4'-diphenylmethanebismaleimide, an epoxy resin and a phenolic resin both shown below and used in the amounts shown in Tables 1 to 3, triphenylphosphine and dicumyl peroxide curing catalysts in the amounts shown in Tables 1 to 3, 260 parts of quartz powder, 1.5 parts of γ -glycidoxy-

EP 0 507 603 B1

propyltrimethoxysilane, 1.5 parts of wax E, and 1.0 part of carbon black.

[0052] These compositions were examined by the following tests (A) to (F). The results are shown in Tables 1 to 3.

(A) Spiral flow

[0053] Using a mold according to the EMMI standard, measurement was made at 175°C and 70 kg/cm².

(B) Flexural strength and Flexural modulus

[0054] Test bars of 10 × 4 × 100 mm which were molded at 180°C and 70 kg/cm² for 2 minutes and post cured at 180°C for 4 hours were tested at 215°C according to JIS K6911.

(C) Coefficient of linear expansion (α) and Glass transition temperature (T_g)

[0055] Using a dilatometer, test pieces of 4 mm in diameter and 15 mm long were examined by heating the test pieces at a rate of 5°C/min.

(D) Crack resistance upon soldering after moisture absorption

[0056] Silicon chips of 2 × 6 × 0.3 mm were bonded to SO package frames of 4 × 12 × 1.8 mm and then encapsulated with the thermosetting resin compositions by molding at 175°C for 2 minutes and post curing at 180°C for 4 hours. The packages were allowed to stand in a hot humid atmosphere at 85°C and RH 85% for 24 and 48 hours and then immersed for 10 seconds in a solder bath at 240°C. Then the packages were disintegrated to observe the occurrence of internal cracks. Reported is the number of cracked packages/the total number of packages tested.

(E) Moisture resistance

[0057] 4-M DRAM chips were bonded to SOJ frames with 20 pins and then encapsulated with the thermosetting resin compositions by molding at 180°C for 2 minutes and post curing at 180°C for 4 hours. The packages were allowed to stand for 24 hours in a hot humid atmosphere at 121°C and RH 100%, then dipped for 10 seconds in a solder bath at 260°C, and again allowed to stand for 300 hours in a hot humid atmosphere at 121°C and RH 100%. Reported is the number of Al wire broken packages/the total number of packages tested.

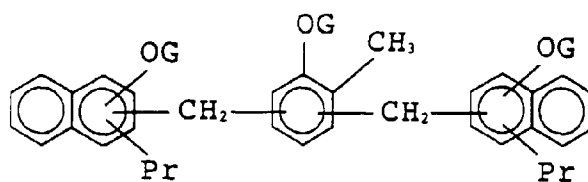
(F) Water absorption

[0058] Disks of 50 mm in diameter and 3 mm thick were molded at 180°C and 70 kg/cm² for 2 minutes and post cured at 180°C for 4 hours. The disks were subjected to a pressure cooker test (PCT) at 121°C /100% RH for 24 hours before the water absorption (percent) was measured.

Epoxy resin

Epoxy equiv.	Softening point(°C)
-----------------	------------------------

(1)

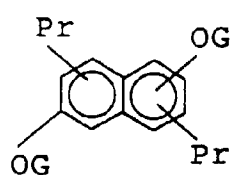


232

90

(designated Compound I)

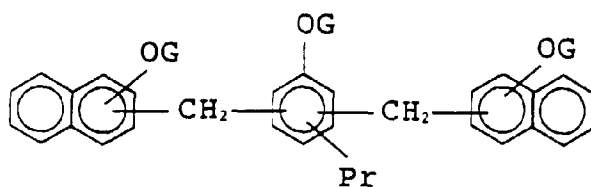
(2)



188

80

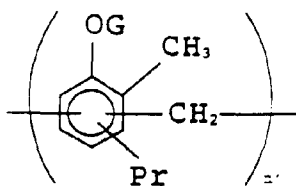
(3)



176

85

(4)



239

70

(5) Cresol novolak type epoxy resin
EOCN-1020-65 (Nihon Kayaku K.K.)

198

65

(6) Brominated epoxy resin
BREN-S (Nihon Kayaku K.K.)

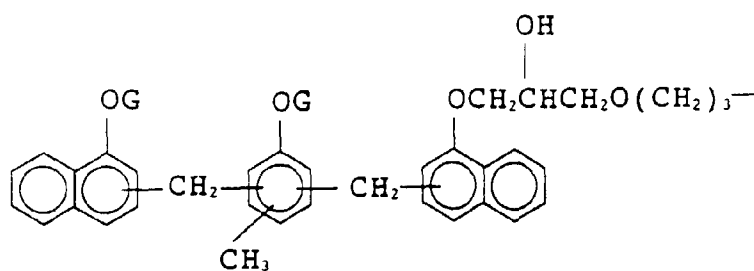
280

80

Epoxy resin

Epoxy equiv.	Softening point (°C)
1800	95
910	85

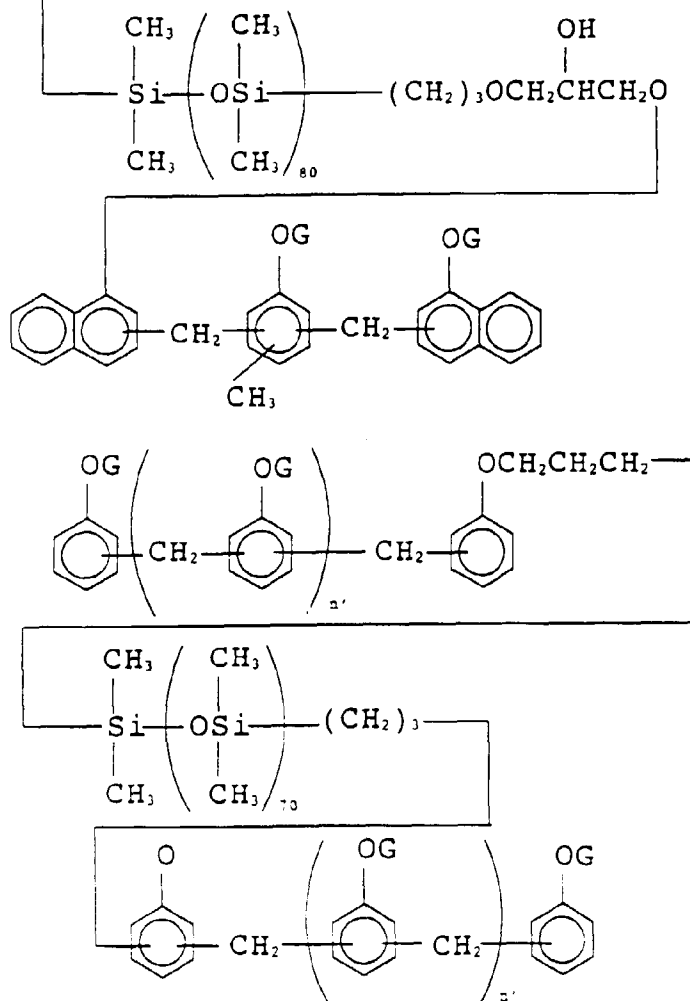
(7)



1800

95

(8)



910

85

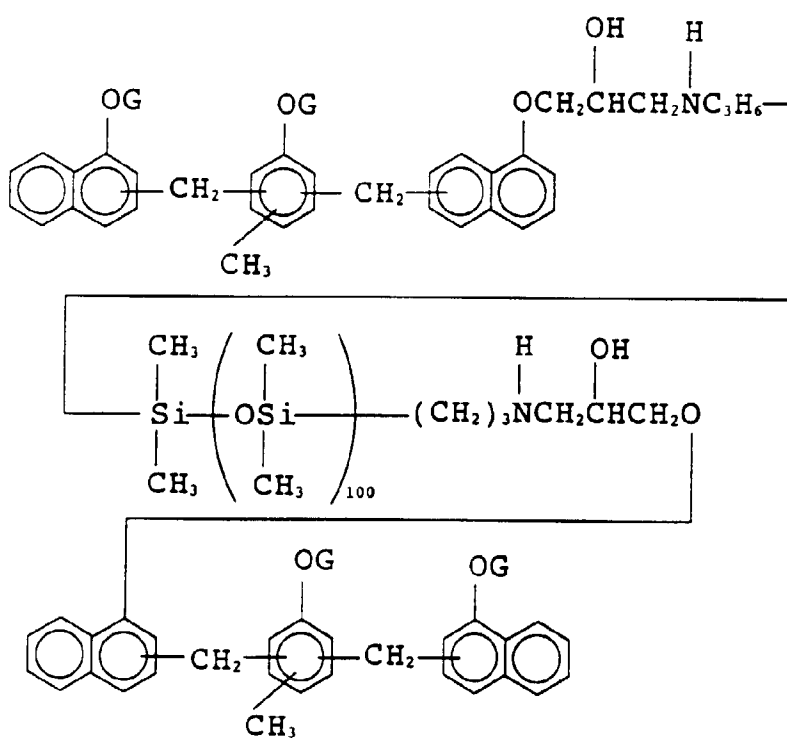
Epoxy resin

Epoxy equiv.	Softening point (°C)
-----------------	-------------------------

(9)

2180

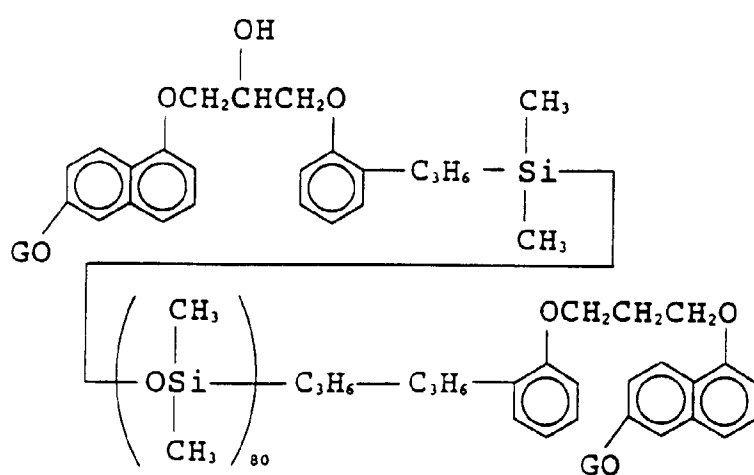
94



(10)

340

84



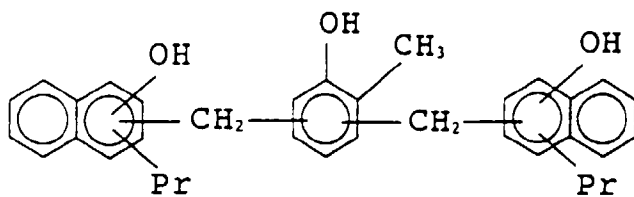
G is $-\text{CH}_2\text{CH}-\text{CH}_2-$, Pr is $-\text{CH}=\text{CH}-\text{CH}_3-$,

n' is 3 on average.

Phenolic resinOH
equiv.

(11)

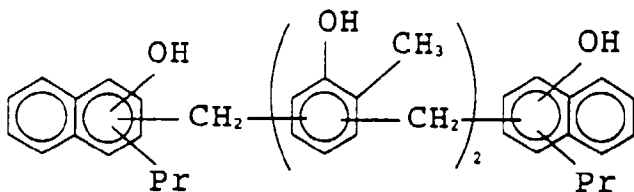
169



(designated Compound H)

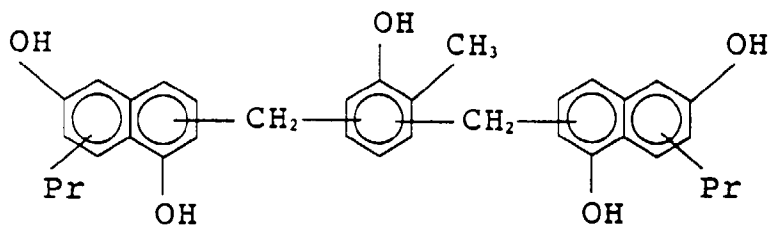
(12)

149



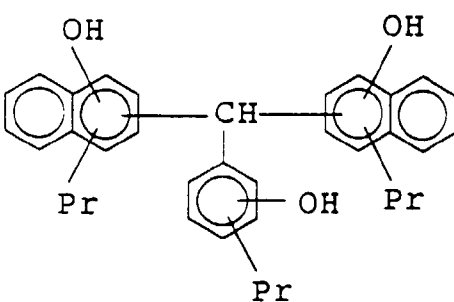
(13)

101



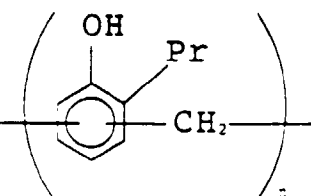
(14)

166



(15)

150



(16) Phenol novolak resin
KH3488 (Dai-Nihon Ink K.K.)

110

Pr is $-\text{CH}=\text{CH}-\text{CH}_3$, and n is 2 to 7.

Table 1

	Example				Comparative Example		
	1	2	3	4	1	2	3
N,N' - 4,4' - diphenylmethanebismaleimide	30	30	30	30	30	30	—
Epoxy resin (1)	12.3	42.5	—	35.6	—	—	—
Epoxy resin (2)	—	—	39.7	—	—	—	—
Epoxy resin (3)	—	—	—	—	—	—	—
Epoxy resin (4)	30.7	—	—	—	42.9	36.5	53.2
Epoxy resin (6)	6.0	6.0	6.0	6.0	6.0	6.0	6.0
Phenolic resin (11)	—	—	—	28.2	—	—	40.8
Phenolic resin (15)	—	—	—	—	—	7.5	—
Phenolic resin (16)	21.0	21.5	24.3	—	21.1	—	—
Triphenyl phosphine	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Dicumyl peroxide	0.4	0.4	0.4	0.4	0.4	0.4	—
Spiral flow, inch	33	32	34	33	34	31	32
Flexural strength, kg/mm ²	3.2	3.4	3.1	3.3	1.7	2.0	2.1
Flexural modulus, kg/mm ²	198	205	201	202	220	212	215
Tg, °C	210	225	225	230	190	215	170
μ , 10 ⁻⁵ /°C	1.61	1.60	1.62	1.61	1.81	1.79	1.80
Crack resistance	85°C/85% RH 24 hr.				20/20 20/20 12/20		
	85°C/85% RH 48 hr.				— — —		
Moisture resistance	0/40	0/40	0/40	0/40	40/40	40/40	30/40
Water absorption, %	0.51	0.52	0.53	0.49	0.71	0.70	0.55

Table 2

	Example											
	5	6	7	8	9	10	11	12				
N,N' - 4,4' - diphenylmethanebismaleimide	30	30	30	30	30	30	30	30				
Epoxy resin (1)	35.3	27.9	29.1	35.0	35.3	35.4	31.3	36.3				
Epoxy resin (6)	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0				
Epoxy resin (7)	10	—	10	—	—	—	10	10				
Epoxy resin (8)	—	11	—	11	—	—	—	—				
Epoxy resin (9)	—	—	—	—	10	—	—	—				
Epoxy resin (10)	—	—	—	—	—	10	—	—				
Phenolic resin (11)	—	25.1	24.9	—	—	—	—	—				
Phenolic resin (12)	—	—	—	—	—	—	22.9	—				
Phenolic resin (13)	—	—	—	—	—	—	—	17.7				
Phenolic resin (16)	18.7	—	—	18.5	18.7	18.6	—	—				
Triphenyl phosphine	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0				
Dicumyl peroxide	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4				
Spiral flow, inch	31	30	32	31	30	31	29	32				
Flexural strength, kg/mm ²	3.2	3.4	3.1	3.3	3.2	3.0	3.1	3.0				
Flexural modulus, kg/mm ²	118	135	128	122	125	119	118	125				
Tg, °C	210	220	220	215	218	221	220	221				
μ , 10 ⁻⁵ /°C	1.40	1.40	1.42	1.41	1.41	1.42	1.40	1.42				
Crack resistance	85°C/85% RH 24 hr.											
	0/20 0/20 0/20 0/20 0/20 0/20 0/20 0/20											
Moisture resistance	85°C/85% RH 48 hr.											
	0/40 0/40 0/40 0/40 0/40 0/40 0/40 0/40											
Water absorption, %	0.58	0.52	0.50	0.55	0.56	0.53	0.51	0.52				

Table 3

	Example		Comparative		
	13	14	4	5	6
N,N' - 4,4' - diphenylmethanebismaleimide	30	30	30	—	—
Epoxy resin (1)	29.6	31.1	—	—	—
Epoxy resin (3)	—	—	—	50.2	—
Epoxy resin (4)	—	—	33.5	—	53.1
Epoxy resin (6)	6.0	6.0	6.0	6.0	6.0
Epoxy resin (7)	10	10	10	10	10
Phenolic resin (14)	24.4	—	—	—	—
Phenolic resin (15)	—	23.0	—	33.8	—
Phenolic resin (16)	—	—	20.5	—	30.9
Triphenyl phosphine	1.0	1.0	1.0	1.0	1.0
Dicumyl peroxide	0.4	0.4	0.4	—	—
Spiral flow, inch	31	30	29	30	29
Flexural strength, kg/mm ²	3.5	3.4	1.7	1.6	1.5
Flexural modulus, kg/mm ²	130	128	130	140	142
Tg, °C	225	223	206	165	164
μ , 10 ⁻⁵ /°C	1.41	1.42	1.41	1.45	1.44
Crack resistance	85°C/85% RH 24 hr.		20/20	2/20	3/20
	85°C/85% RH 48 hr.		—	20/20	20/20
Moisture resistance	0/40	0/40	25/40	36/40	35/40
Water absorption, %	0.56	0.57	0.70	0.51	0.53

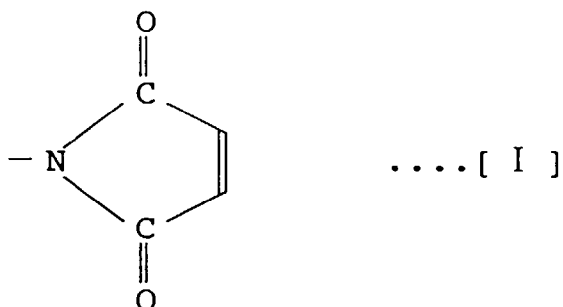
[0059] As seen from Tables 1 to 3, thermosetting resin compositions in which an imide compound having a maleimide group is blended with resins having a double bond conjugated with an aromatic group and a naphthalene ring (Examples 1 to 15) are improved in Tg, flexural strength at high temperature, crack resistance, moisture resistance and water absorption over thermosetting resin compositions free of such a double bond or naphthalene ring-containing resin

(Comparative Examples 1 to 6).

Claims

1. A thermosetting resin composition comprising

(A) an imide compound having a maleimide group of the general formula [I]:



(B) a resin having at least two epoxy groups in a molecule, and

(C) a resin having a phenolic hydroxyl group in a molecule

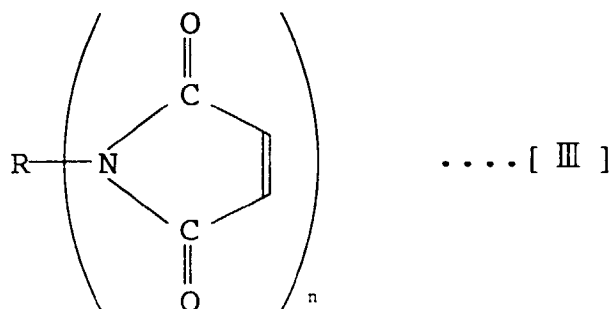
wherein resin (B) has a double bond conjugated with a naphthalene ring.

2. A thermosetting resin composition of claim 1 which further comprises (D) a copolymer obtainable by reacting an aromatic polymer with an organopolysiloxane having the compositional formula [II]:



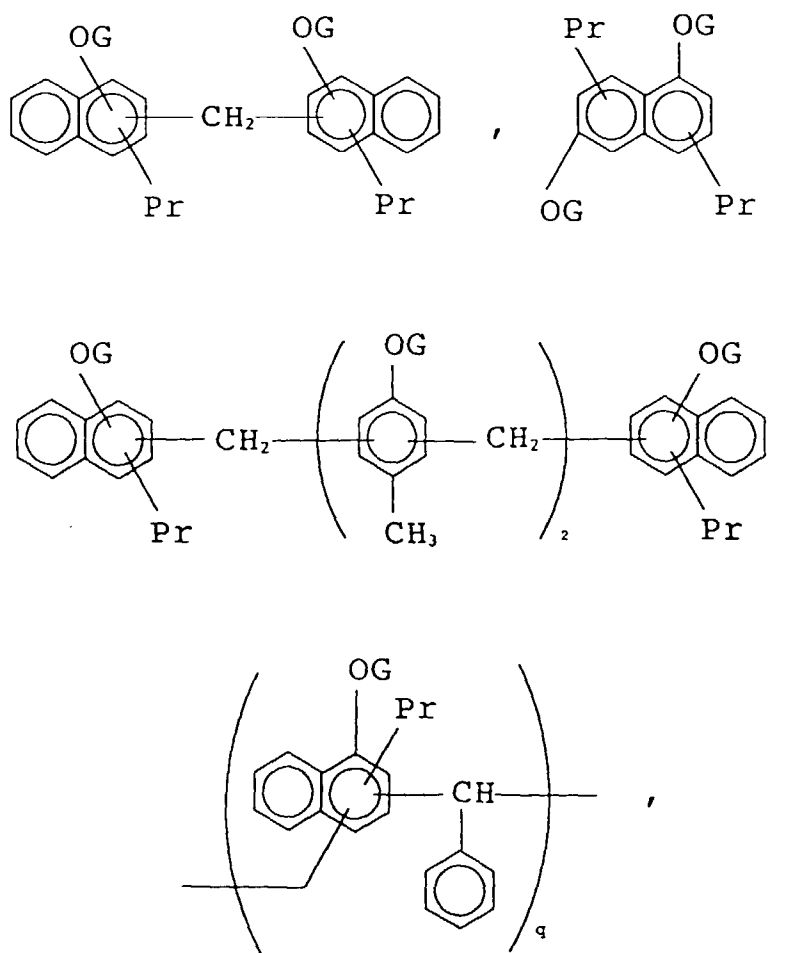
wherein R^1 is a hydrogen atom, hydroxyl group, alkoxy group, or monovalent organic group containing an amino, epoxy, hydroxyl or carboxyl group, R^2 is a substituted or unsubstituted monovalent organic group, and letters a and b are positive numbers satisfying $0.001 \leq a \leq 1$, $1 \leq b \leq 3$, and $1.001 \leq a + b \leq 4$, and wherein the number of silicon atoms said organopolysiloxane has in its molecule is an integer of 1 to 1000 and the number of functional groups represented by R^1 directly attached to silicon atoms of said organopolysiloxane in its molecule is an integer of at least 1.

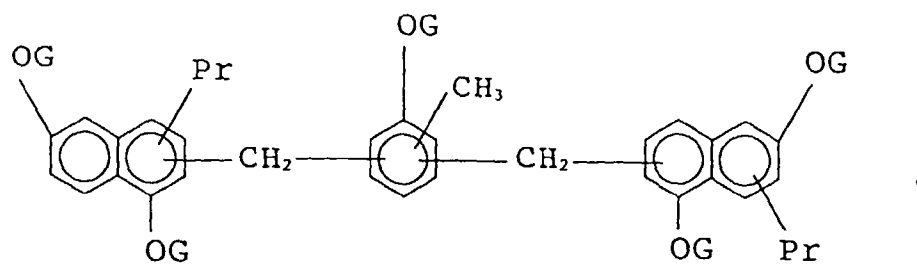
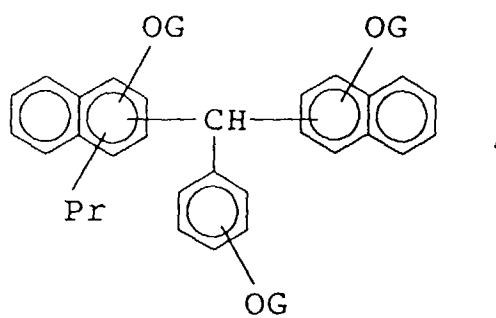
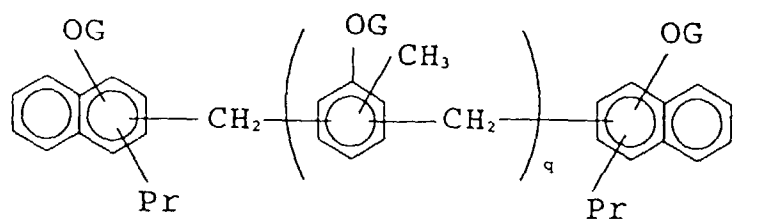
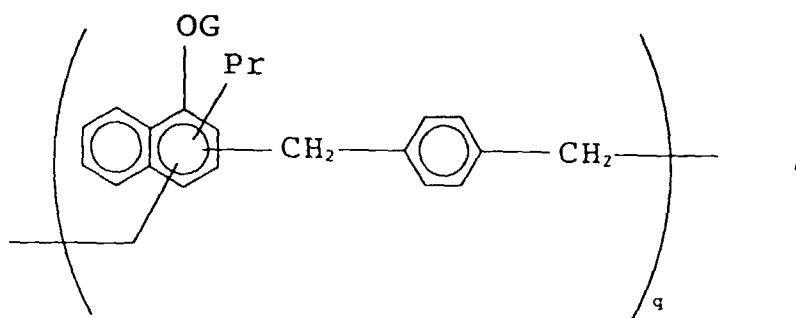
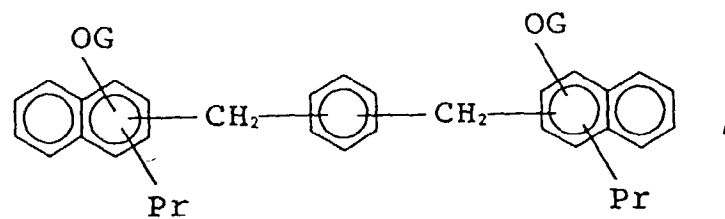
3. A composition of claim 1 or 2 wherein the imide compound is a compound having an N-substituted maleimide group of the formula [III]:



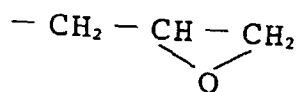
wherein R is an n-valent organic group and n is an integer of from 1 to 20.

4. A composition of claim 1 or 2 wherein the imide compound is selected from the group consisting of N-substituted trimaleimides and N-substituted bismaleimides.
5. A composition of any preceding claim wherein component (c) is a phenolic resin having at least one double bond conjugated with an aromatic ring, and at least one naphthalene ring.
6. A composition according to claim 5 in which in the phenolic resin component (C) the double bond is conjugated with the naphthalene ring.
7. A composition of any preceding claim wherein components (B) and (C) are present in a total amount of about 20 to about 400 parts by weight per 100 parts by weight of component (A).
8. A composition of any preceding claim wherein components (B) and (C) together contain at least about 10% by weight of naphthalene ring based on their total weight.
9. A composition according to any one of the preceding claims in which the double bond conjugated with naphthalene ring is that of a propenyl group.
10. A composition according to claim 9 in which the epoxy resin component (B) is selected from the following:





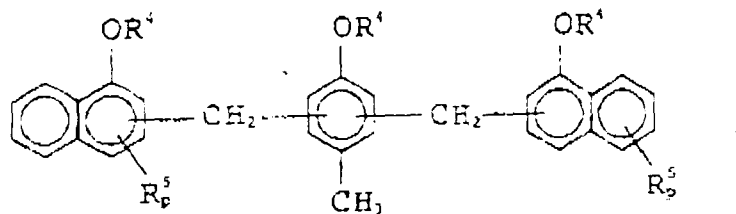
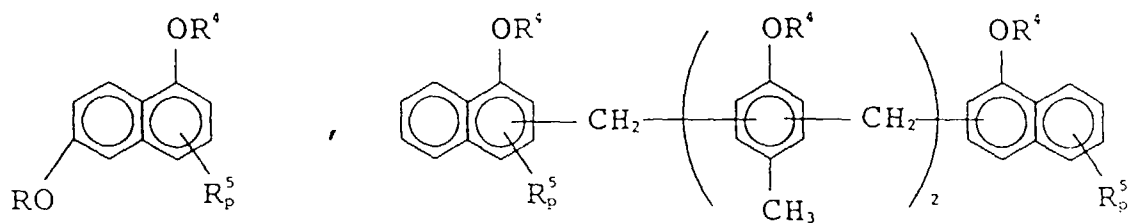
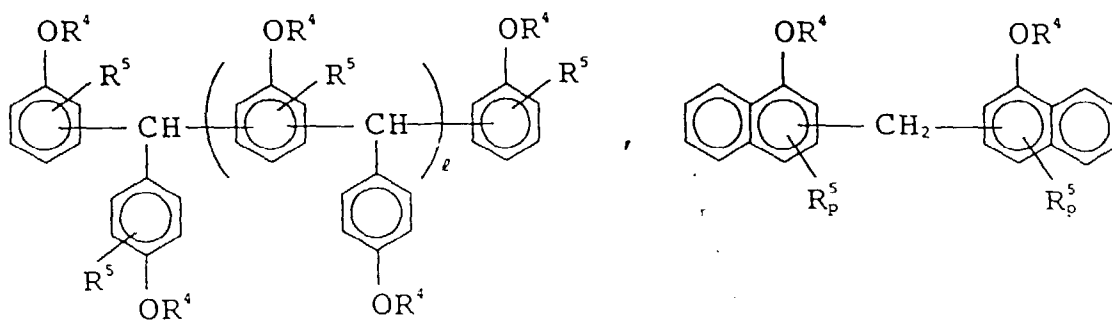
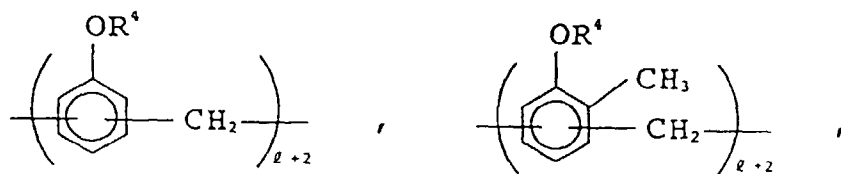
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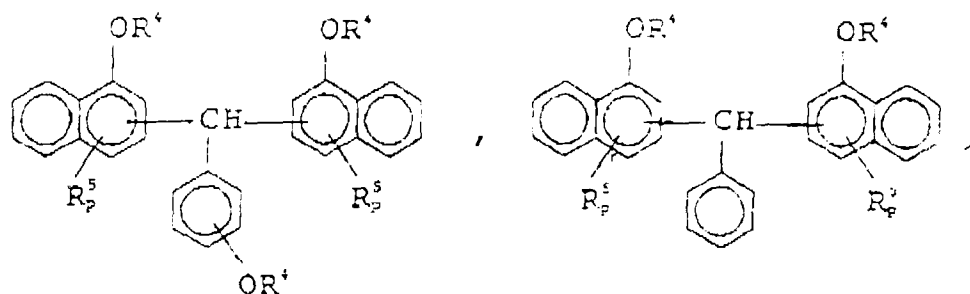
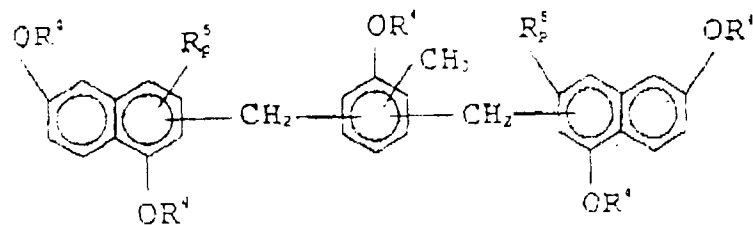
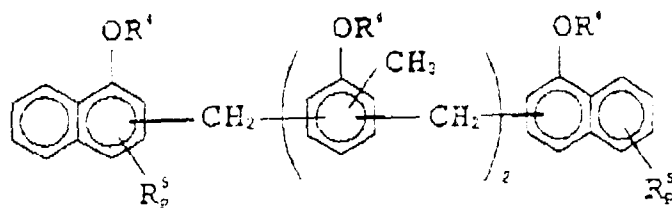
Pr: -CH=CH-CH₃

q: an integer of from 2 to 10

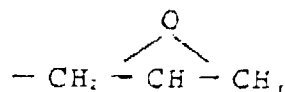
11. A composition according to claim 2 in which:

the aromatic polymer is selected from compounds having the following structural units.

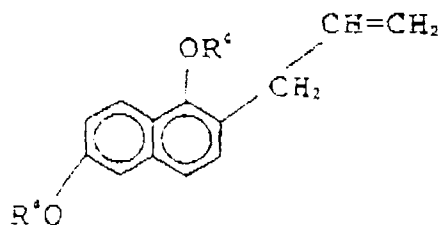




Where R^4 is a hydrogen atom or



and R^2 is independently selected from alkyl groups having 1 to 10 carbon atoms, ℓ is an integer of from 0 to 4, and p is an integer of from 0 to 2,





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where each of s and t is an integer of from 1 to 6;

and substituted R² is a substituted or unsubstituted monovalent organic group having 1 to 10 carbon atoms, such as an alkyl group such as methyl, ethyl, propyl, or butyl group; an alkenyl group such as vinyl or allyl group;

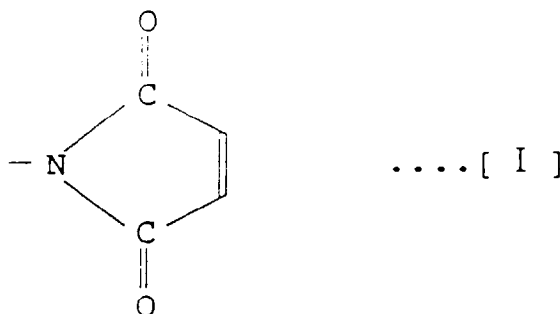
a cycloalkyl groups such as a cyclohexyl group; an aryl group such as a phenyl or a tolyl group; an aralkyl group such as a benzyl or a phenylethyl group; and substituted ones thereof in which some or all of the hydrogen atoms are replaced by halogen atoms or chloromethyl and 3,3,3-trifluoropropyl groups.

12. A method comprising the preparation of a composition according to any one of claims 1 to 11.
13. Use of a composition according to any one of claims 1 to 11 for moulding, coating, encapsulating or as an adhesive.
14. An article moulded from or comprising a coating or encapsulation of a composition according to any one of claims 1 to 11.

Patentansprüche

1. Wärmehärtende Harzzusammensetzung, umfassend:

(A) eine Imidverbindung mit einer Maleimidgruppe der allgemeinen Formel [I]:



(B) ein Harz mit zumindest zwei Epoxygruppen pro Molekül und

(C) ein Harz mit einer phenolischen Hydroxylgruppe pro Molekül,

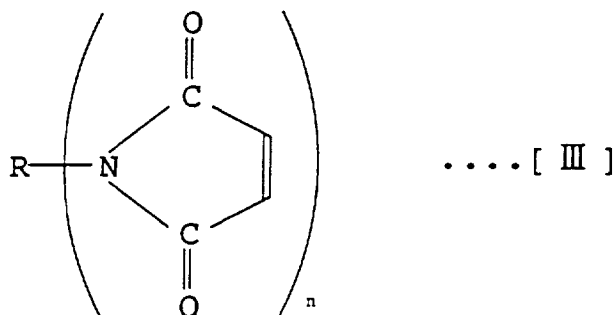
worin das Harz (B) eine Doppelbindung aufweist, die mit einem Naphthalinring konjugiert ist.

2. Wärmehärtende Harzzusammensetzung nach Anspruch 1, die weiters (D) ein Copolymer umfaßt, das durch Umsetzen eines aromatischen Polymers mit einem Organopolysiloxan der Formel [II]



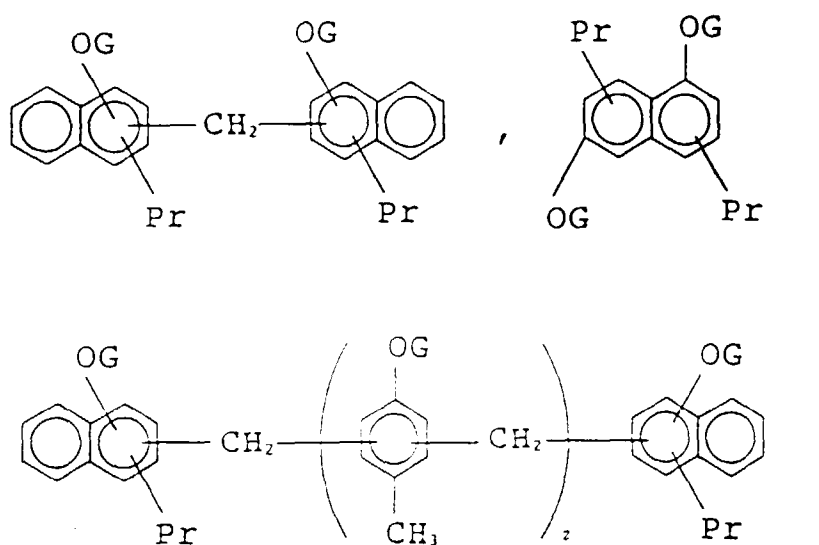
erhältlich ist, worin R^1 ein Wasserstoffatom, eine Hydroxylgruppe, eine Alkoxygruppe oder eine einwertige organische Gruppe ist, die eine Amino-, Epoxy-, Hydroxyl- oder Carboxylgruppe enthält, R^2 eine substituierte oder unsubstituierte, einwertige, organische Gruppe ist und die Buchstaben a und b positive Zahlen sind, für die gilt $0,001 \leq a \leq 1$, $1 \leq b \leq 3$ und $1,001 \leq a + b \leq 4$, und worin die Anzahl an Siliziumatomen, die das Organopolysiloxan im Molekül aufweist, eine ganze Zahl von 1 bis 1.000 ist und die Anzahl an durch R^1 dargestellten funktionellen Gruppen, die direkt an Siliziumatome des Organopolysiloxans in dessen Molekül gebunden sind, eine ganze Zahl von zumindest 1 ist.

3. Zusammensetzung nach Anspruch 1 oder 2, worin die Imidverbindung eine Verbindung mit einer N-substituierten Maleimidgruppe der Formel [III]



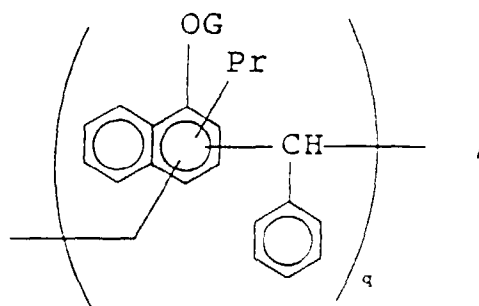
15 ist, worin R eine n-wertige organische Gruppe ist und n eine ganze Zahl von 1 bis 20 ist.

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4. Zusammensetzung nach Anspruch 1 oder 2, worin die Imidverbindung aus der aus N-substituierten Trimaleimiden und N-substituierten Bismaleimiden bestehenden Gruppe ausgewählt ist.
 5. Zusammensetzung nach einem der vorangegangenen Ansprüche, worin Komponente (C) ein Phenolharz mit zumindest einer Doppelbindung, die mit einem aromatischen Ring konjugiert ist, und zumindest einem Naphthalinring ist.
 6. Zusammensetzung nach Anspruch 5, worin in der Phenolharzkomponente (C) die Doppelbindung mit dem Naphthalinring konjugiert ist.
 7. Zusammensetzung nach einem der vorangegangenen Ansprüche, worin die Komponenten (B) und (C) in einer Gesamtmenge von etwa 20 bis etwa 400 Gewichtsteilen pro 100 Gewichtsteile von Komponente (A) vorhanden sind.
 8. Zusammensetzung nach einem der vorangegangenen Ansprüche, worin die Komponenten (B) und (C) zusammen, bezogen auf ihr Gesamtgewicht, zumindest etwa 10 Gew.-% Naphthalinringe enthalten.
 9. Zusammensetzung nach einem der vorangegangenen Ansprüche, bei der die mit Naphthalinring konjugierte Doppelbindung die einer Propenylgruppe ist.
 10. Zusammensetzung nach Anspruch 9, bei der die Epoxyharzkomponente (B) aus den folgenden ausgewählt ist:



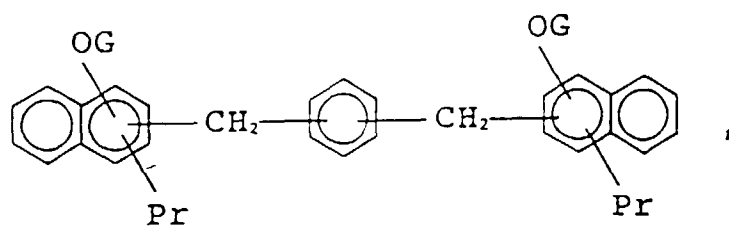
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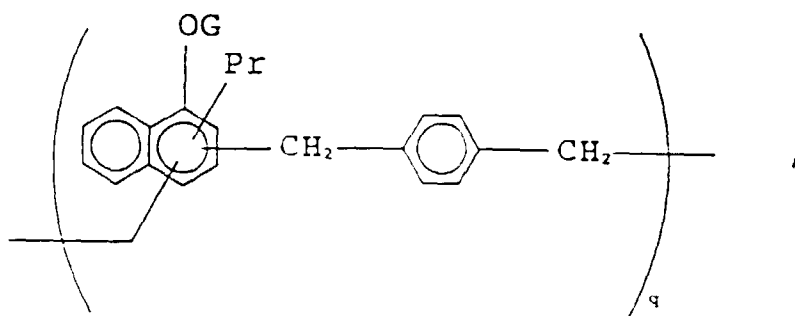
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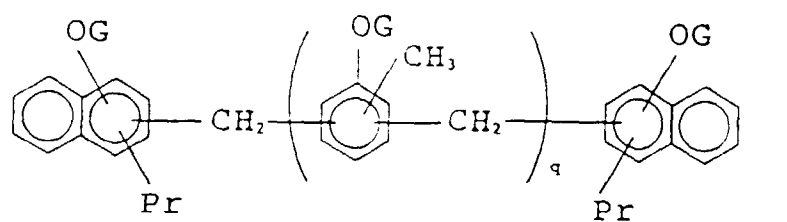
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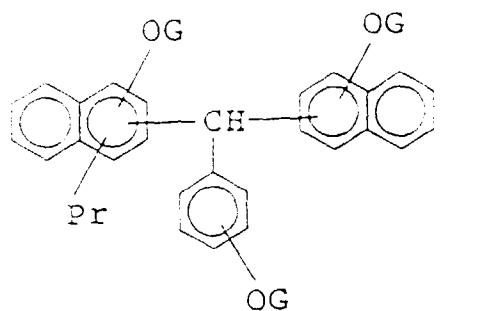
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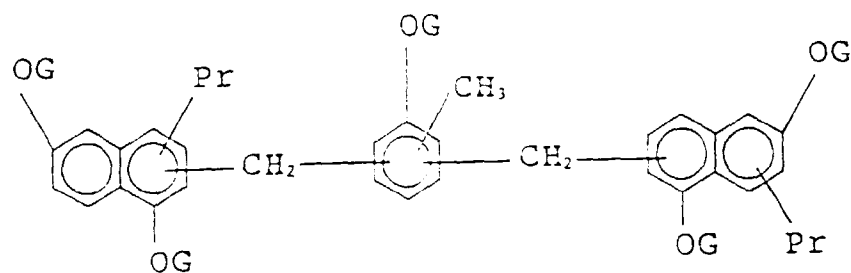
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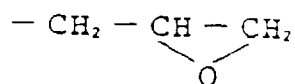
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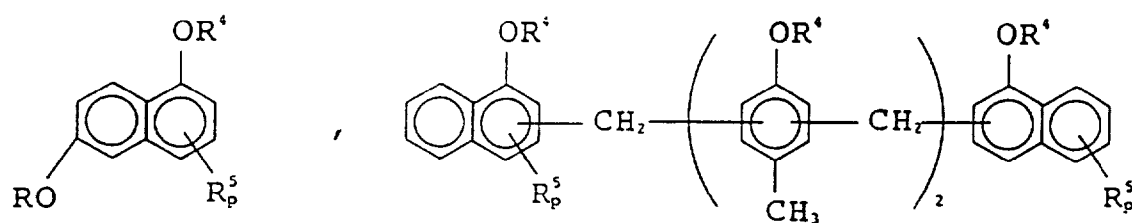
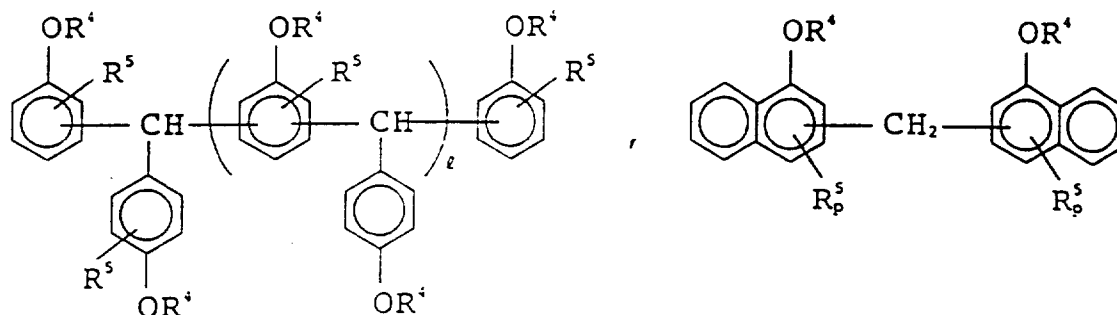
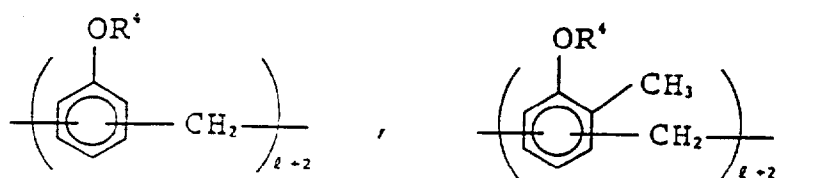


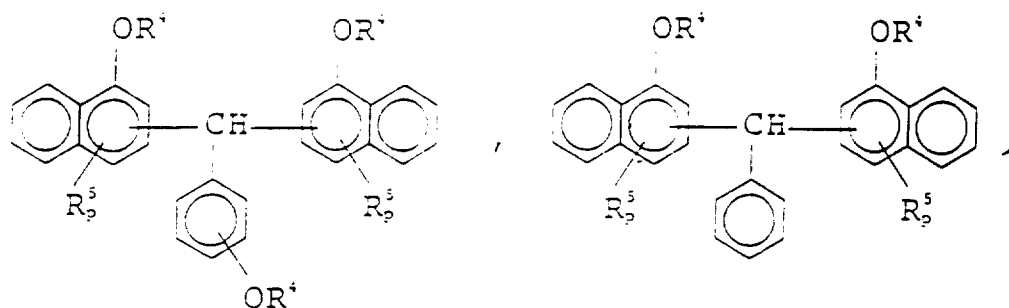
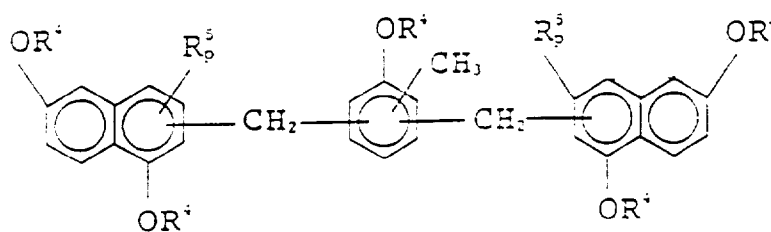
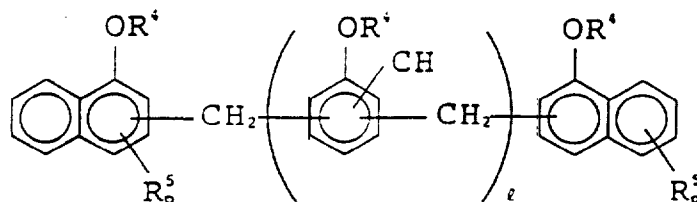
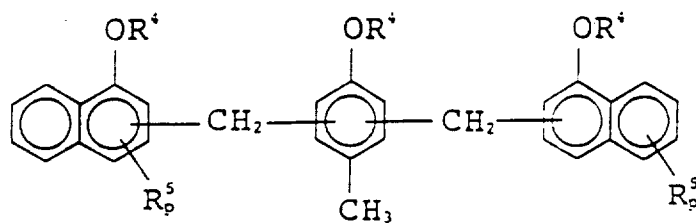
G:

Pr: -CH=CH-CH₃

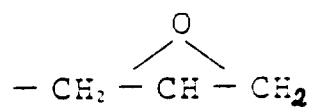
q: eine ganze Zahl von 2 bis 10.

11. Zusammensetzung nach Anspruch 2, bei der das aromatische Polymer aus Verbindungen ausgewählt ist, die die folgenden Struktureinheiten aufweisen:

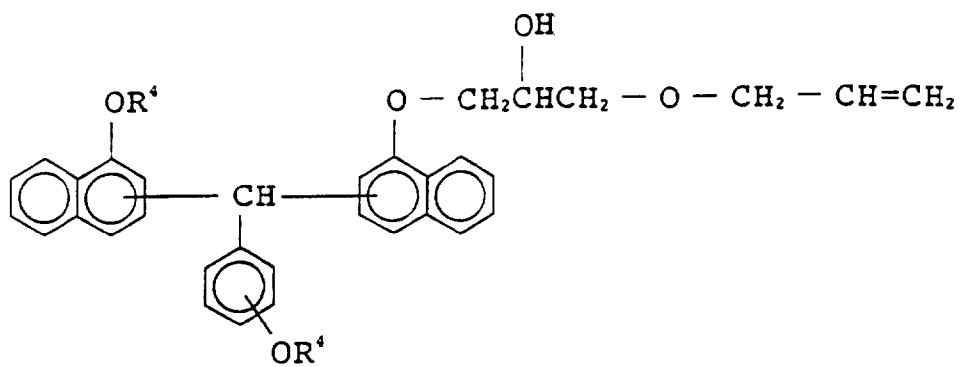
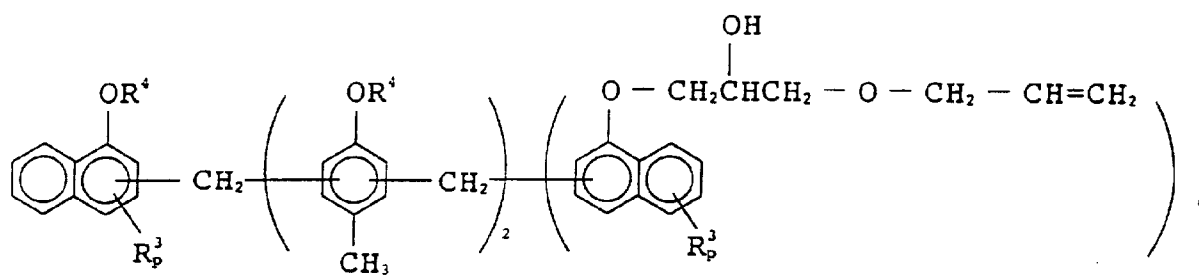
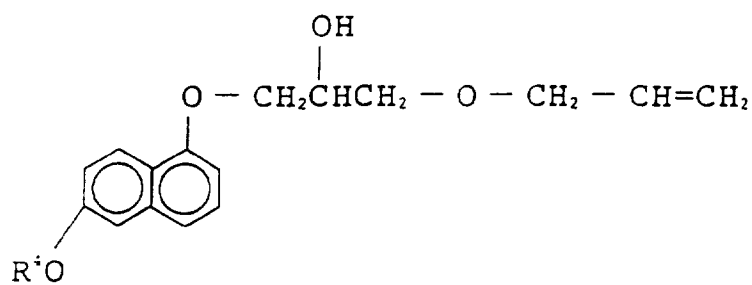
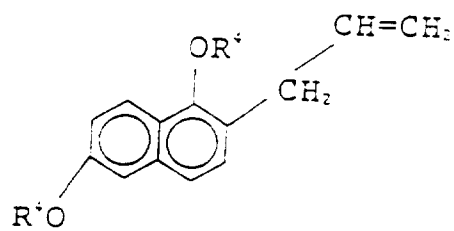


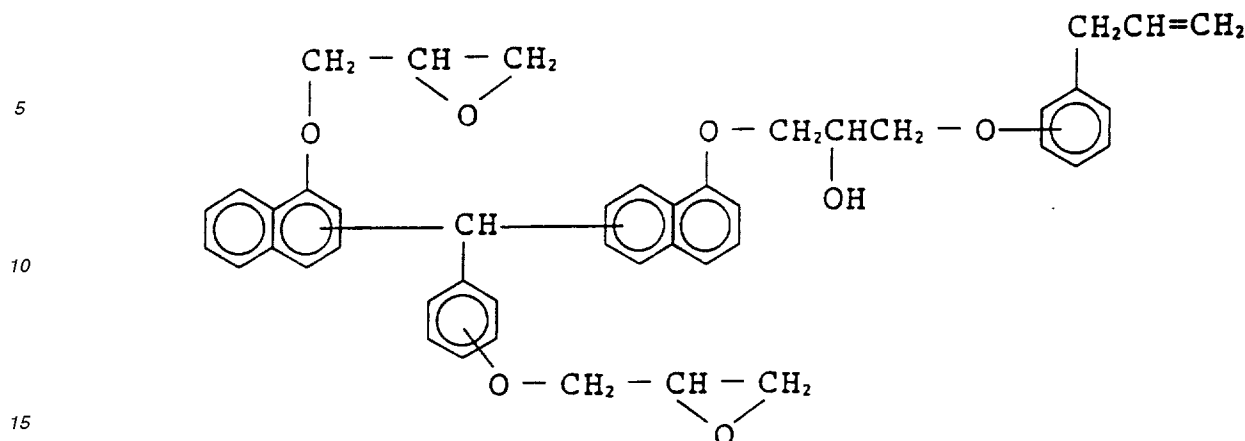


worin R^4 ein Wasserstoffatom oder



ist und R^5 unabhängig voneinander ausgewählt sind aus Alkylgruppen mit 1 bis 10 C-Atomen, l eine ganze Zahl von 0 bis 4 und p eine ganze Zahl von 0 bis 2 ist,





20 worin jedes von s und t eine ganze Zahl von 1 bis 6 ist;

und Substituent R² eine substituierte oder unsubstituierte, einwertige, organische Gruppe ist, die 1 bis 10 Kohlenstoffatome aufweist, wie z.B. eine Alkylgruppe wie die Methyl-, Ethyl-, Propyl- oder Butylgruppe; eine Alkenylgruppe wie die Vinyl- oder Allylgruppe; eine Cycloalkylgruppe wie die Cyclohexylgruppe; eine Arylgruppe wie die Phenyl- oder Tolygruppe; eine Aralkylgruppe wie die Benzyl- oder Phenylethylgruppe, und substituierte Vertreter davon, bei denen einige oder alle Wasserstoffatome durch Halogenatome oder Chlormethyl- und 3,3,3-Trifluorpropylgruppen ersetzt sind.

25 12. Verfahren, umfassend die Herstellung einer Zusammensetzung nach einem der Ansprüche 1 bis 11.

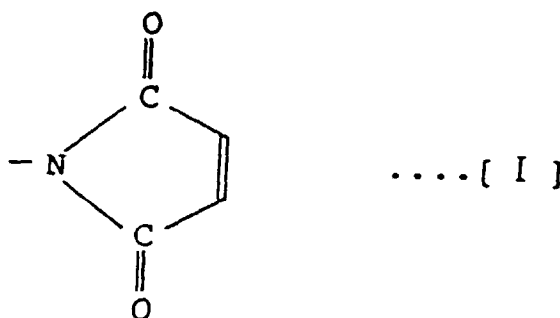
30 13. Verwendung einer Zusammensetzung nach einem der Ansprüche 1 bis 11 zum Formen, Beschichten, Umhüllen oder als Kleber.

14. Gegenstand, der aus einer Zusammensetzung nach einem der Ansprüche 1 bis 11 geformt ist oder einen Überzug oder eine Umhüllung daraus umfaßt.

35 Revendications

1. Composition de résine thermodurcissable comprenant

(A) un composé d'imide ayant un groupe maléïmide de la formule générale [I]:



55 (B) une résine ayant au moins deux groupes époxy dans une molécule, et

(C) une résine ayant un groupe hydroxyle phénolique dans une molécule,

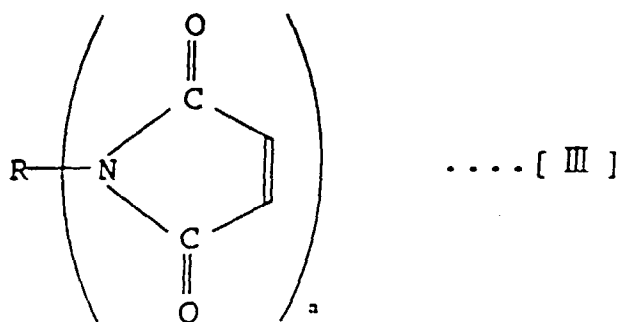
où la résine (B) a une double liaison conjuguée avec un cycle de naphtalène.

2. Composition de résine thermodurcissable de la revendication 1 qui comprend de plus (D) un copolymère pouvant être obtenu par réaction d'un polymère aromatique avec un organopolysiloxane ayant la formule de composition [II]:



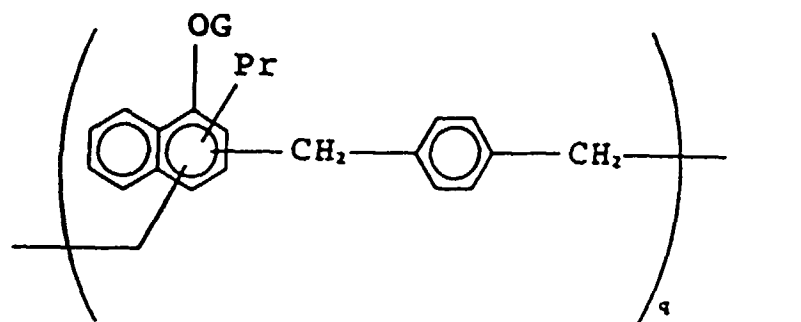
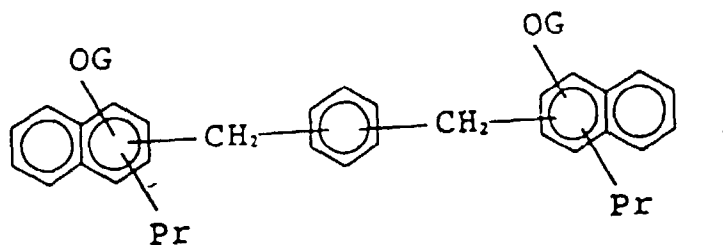
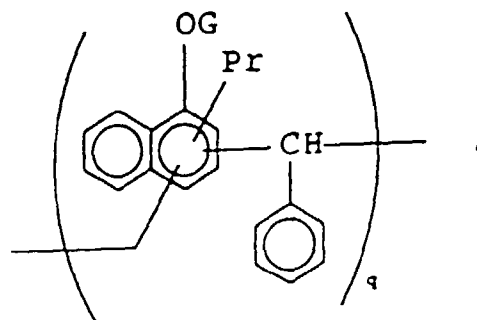
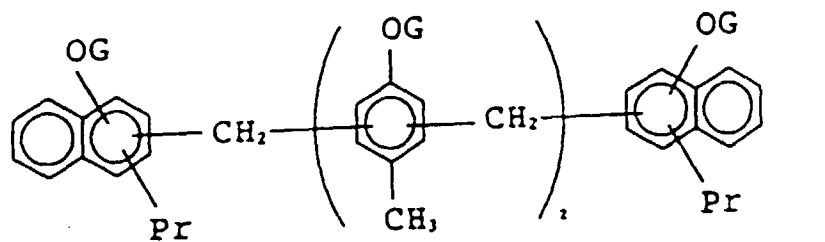
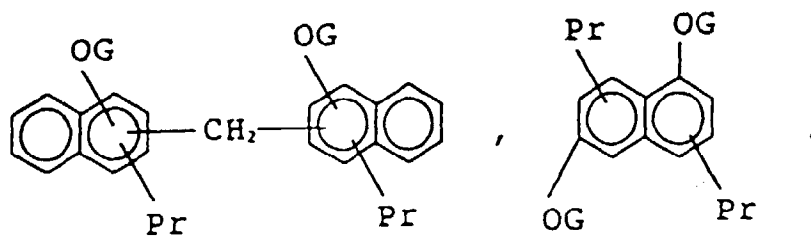
où R^1 est un atome d'hydrogène, un groupe hydroxyle, un groupe alcoxy ou un groupe organique monovalent contenant un groupe amino, époxy, hydroxyle ou carboxyle, R^2 est un groupe organique monovalent substitué ou non substitué et les lettres a et b sont des nombres positifs satisfaisant $0,001 \leq a \leq 1$, $1 \leq b \leq 3$, et $1,001 \leq a + b \leq 4$, et où le nombre des atomes de silicium que ledit organopolysiloxane a dans sa molécule est un entier de 1 à 1000 et le nombre des groupes fonctionnels représentés par R^1 , directement attachés aux atomes de silicium dudit organopolysiloxane dans sa molécule est un entier d'au moins 1.

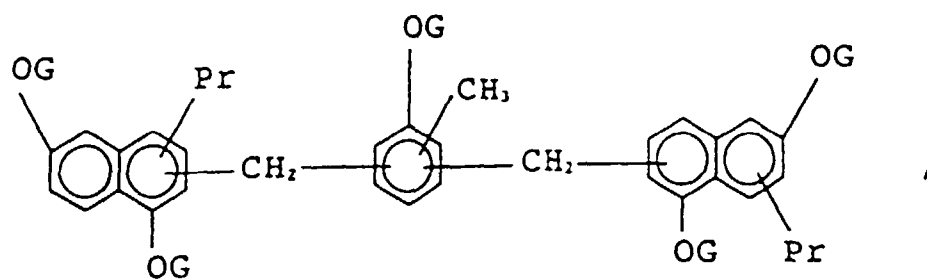
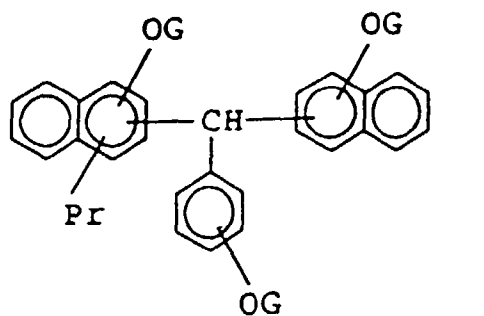
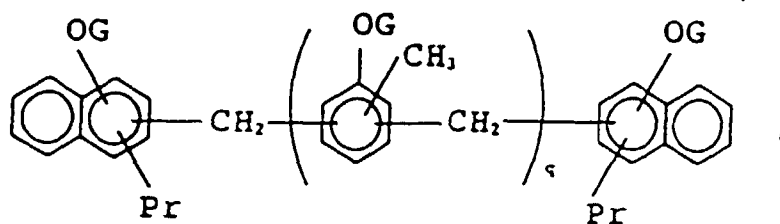
3. Composition de la revendication 1 ou 2 où le composé d'imide est un composé ayant un groupe maléimide N-substitué de la formule [III]:



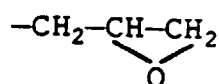
où R est un groupe organique n-valent et n est un entier de 1 à 20.

4. Composition de la revendication 1 ou 2 où le composé d'imide est sélectionné dans le groupe consistant en trimaléimides N-substitués et bismaléimides N-substitués.
5. Composition selon toute revendication précédente où le composant (c) est une résine phénolique ayant au moins une double liaison conjuguée avec un cycle aromatique et au moins un cycle de naphthalène.
6. Composition selon la revendication 5 dans laquelle dans le composant de résine phénolique (C), la double liaison est conjuguée au cycle de naphthalène.
7. Composition de toute revendication précédente où les composants (B) et (C) sont présents en une quantité totale d'environ 20 à environ 400 parties en poids pour 100 parties en poids du composant (A).
8. Composition de toute revendication précédente où les composants (B) et (C) contiennent ensemble au moins environ 10% en poids d'un cycle de naphthalène basé sur leur poids total.
9. Composition selon l'une quelconque des revendications précédentes dans laquelle la double liaison conjuguée avec le cycle de naphthalène est celle d'un groupe propényle.
10. Composition selon la revendication 9 dans laquelle le composant de résine époxy (B) est sélectionné parmi ce qui suit :





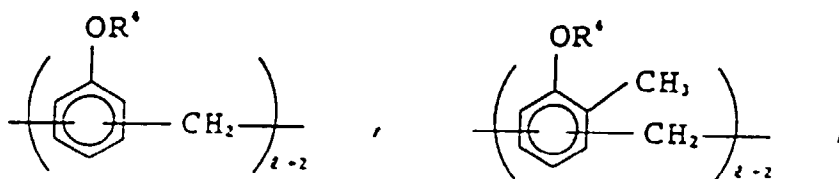
G :

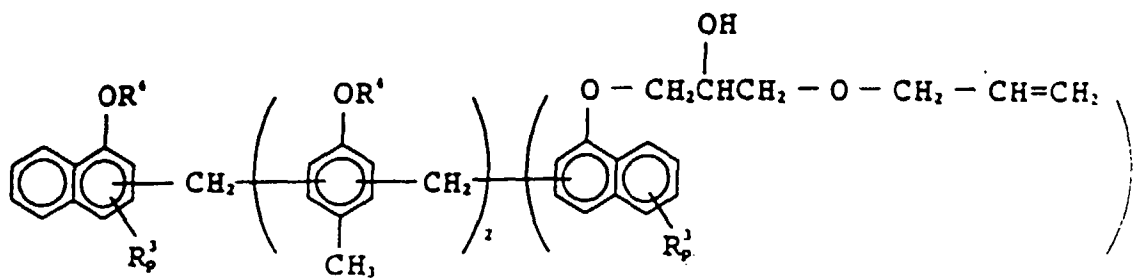
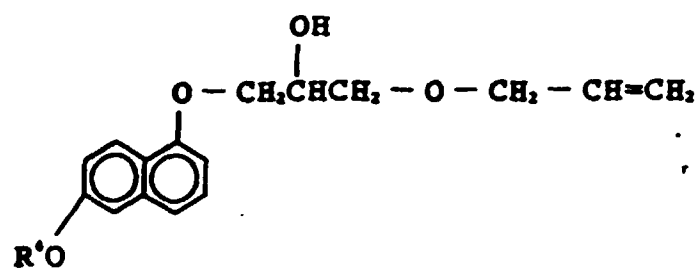
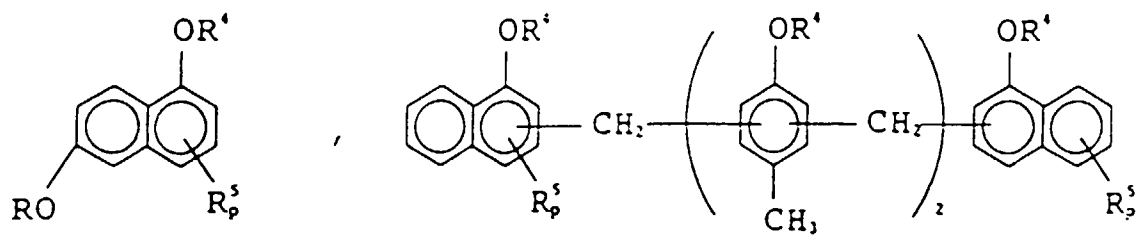
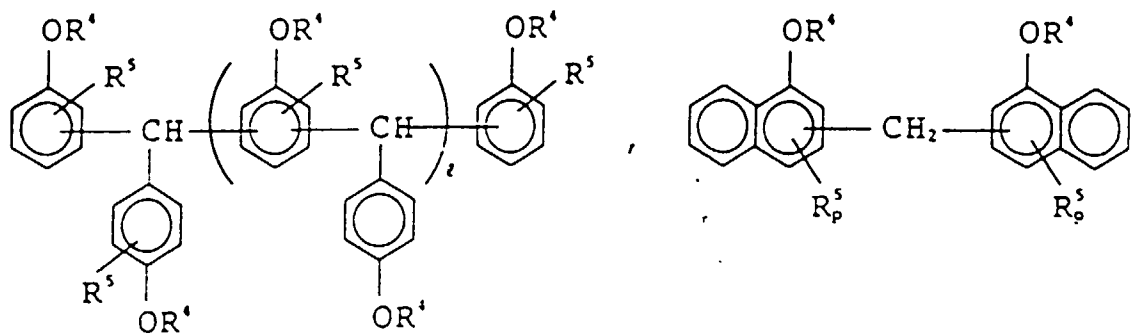
Pr: $\text{CH}=\text{CH}-\text{CH}_3$

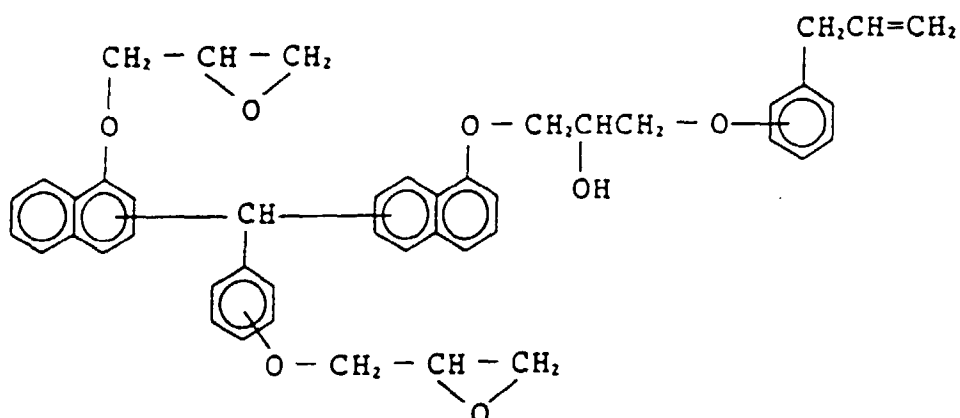
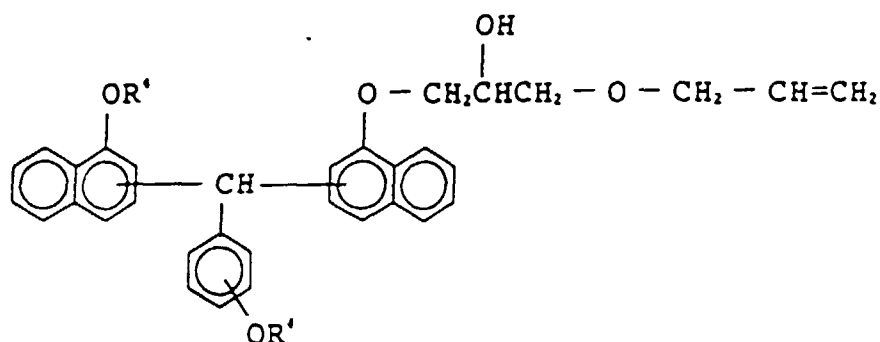
q: un entier de 2 à 10

11. Composition selon la revendication 2 dans laquelle :

le polymère aromatique est sélectionné parmi les composés ayant les unités de structure qui suivent.







où chacun de s et t est un entier de 1 à 6;

et le substituant R^2 est un groupe organique monovalent substitué ou non substitué ayant 1 à 10 atomes de carbone comme un groupe alkyle tel qu'un groupe méthyle, éthyle, propyle, ou butyle; un groupe alcényle tel qu'un groupe vinyle ou allyle; un groupe cycloalkyle tel qu'un groupe cyclohexyle; un groupe aryle tel qu'un groupe phényle ou tolyle; un groupe aralkyle tel qu'un groupe benzyle ou phényléthyle; et ceux qui sont substitués où certains ou tous les atomes d'hydrogène sont remplacés par des atomes d'halogène ou des groupes fluorométhyle et 3,3,3-trifluoropropyle.

12. Méthode comprenant la préparation d'une composition selon l'une quelconque des revendications 1 à 11.

13. Utilisation d'une composition selon l'une quelconque des revendications 1 à 11 pour le moulage, le revêtement, l'encapsulation ou comme adhésif.

14. Article moulé de ou comprenant un revêtement ou une encapsulation d'une composition selon l'une quelconque des revendications 1 à 11.